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Abstract. — A review is given on the determination of the thermodynamic properties of $Si(OC_2H_5)_4$ (TEOS, tetraethoxysilane). In addition, the thermal decomposition of TEOS has been studied by in-situ IR spectroscopy. The decomposition products in the gas phase in the absence of oxygen are organic fragments (ethanol, ethanal, ethene, methane, carbon monoxide), and in the presence of oxygen water, carbon dioxide, ethanal and methanal. The results are compared with thermodynamic equilibrium calculations and kinetic models.

1. Introduction.

Thermodynamic calculations are frequently used to optimize the conditions of CVD processes concerning halide/hydrogen precursors. In the field of organometallic precursors such efforts have only been done for some methyl-substituted compounds such as $Al(CH_3)_3$, and $Cd(CH_3)_3$. Since thermodynamic properties of larger organometallic compounds are rather scarce, optimization by thermodynamic calculations have not been performed yet.

Tetraethoxysilane (TEOS) is an interesting material for the Chemical Vapour Deposition (CVD) of thin silicon dioxide films. The lower temperature needed for the CVD process and the absence of aggressive reaction poducts are the main advantages of using TEOS instead of the traditional precursors, silane or tetrachlorosilane. In addition, the mechanical and electrical properties of SiO_2 films deposited from TEOS are very good.

For TEOS we recently measured the low-temperature heat capacity of the solid/liquid phase, the enthalpy of formation of the liquid, the vapour pressure, and the IR and Raman spectra of the gas phase. These data allow us to evaluate the thermodynamic properties of TEOS in the condensed phase as well as in the gas phase. In addition, its thermal decomposition has been studied by in-situ infrared spectroscopy, and will be discussed in this paper.

2. Experimental.

TEOS (Merck) was distilled twice before use. The fraction boiling at $(166.5 \pm 0.5)°C$ was used. The purity of the sample was checked with NMR. The ^1H NMR showed two peaks at 1.11 ppm (3 Hs, triplet) and 3.75 ppm (2 Hs, quartet). No additional lines of organic impurities were found.

For a detailed description of the experimental conditions of the measurements of the low-temperature heat capacity, the enthalpy of formation, the vibrational frequencies, and the vapour pressure, see references 1–4.

The thermal decomposition was studied by in-situ infrared spetroscopy using a laboratory-built optical cell. The main body of the cell consists of a silica tube (95 cm × 6 cm i.d.) and is heated in a 62.5 cm long furnace which is divided into three independently controllable sections. By heating the outer sections to a higher temperature, a zone of constant temperature can be created in the centre of the furnace. Temperature measurements and control are done by three chromel-alumel thermocouples placed at the windings of the zones. Optical windows are mounted in water-cooled flanges at both ends of the tube. For the low pressure experiment the cell was evacuated and loaded with about 0.1 mbar of TEOS. For the experiments at atmospheric pressure the cell was purged with purified argon or oxygen. The pressure was reduced to 375–550 mbar in such a way that a pressure of about 1 bar was reached at the desired reaction temperature. The spectra (500–4000 cm^{-1}) were recorded with a BOMEM DA 3.02 Fourier transform spectrometer equipped with a globar light source, KRS-5 windows and a DTGS detector.

3. Thermodynamic functions of $Si(OC_2H_5)_4(s, l)$.

The low-temperature heat capacity of solid and liquid TEOS has been measured from 5 to 362 K by adiabatic calorimetry [1] (Fig. 1). Two transitions were observed in this temperature range, a solid-to-solid transition at $T = 187.72$ K with $\Delta_{trs}H^o_m = 13.20$ kJ·mol^{-1}, and a solid-to-liquid transition at $T = 190.97$ K with $\Delta_{fus}H^o_m = 11.14$ kJ·mol^{-1} (Fig. 1). The standard entropy of $Si(OC_2H_5)_4(l)$, derived from the low-temperature data, is:

$$S^o_m(298.15 \text{ K}) = (533.1 \pm 1.0) \text{ J·mol}^{-1}\text{·K}^{-1}.$$

The molar heat capacity of liquid TEOS can be described by the function:

$$C^o_{p,m}/\text{J·mol}^{-1}\text{·K}^{-1} = a(T/K)^{-2} + b(T/K) + c.$$
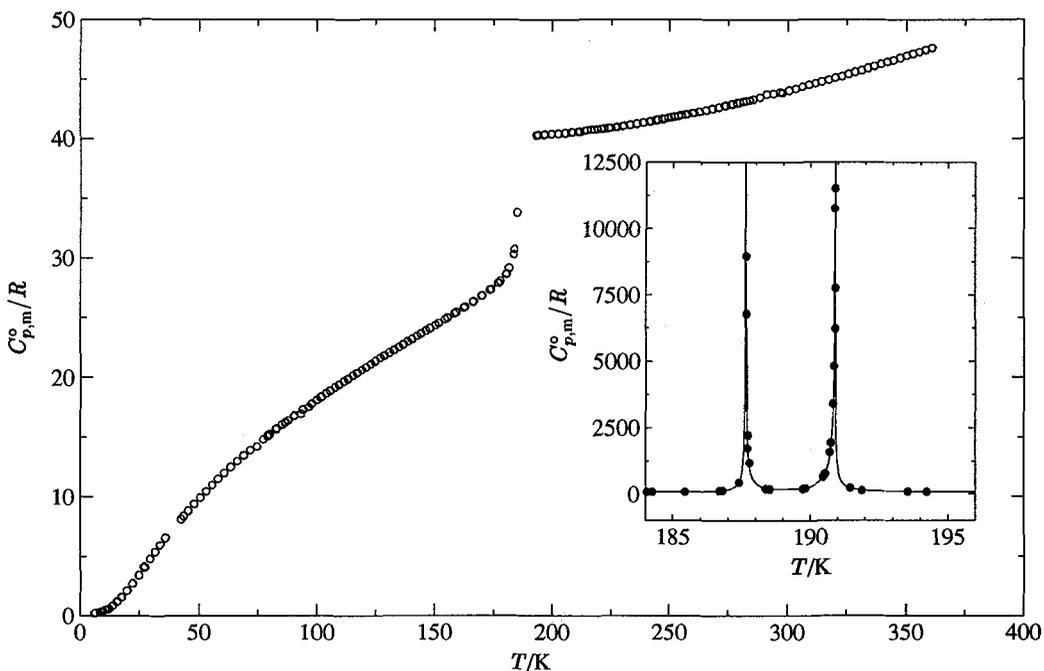

Fig. 1. — Low-temperature heat capacity of tetraethoxysilane.

Table I. — The thermodynamic functions of liquid and gaseous $Si(OC_2H_5)_4$ ($p° = 101.325$ kPa).

T (K)	$C_{p,m}°$ (J·mol⁻¹·K⁻¹)	$\Delta_0^T S_m°$ (J·mol⁻¹·K⁻¹)	$\Phi_m°$ (J·mol⁻¹·K⁻¹)	$\Delta_{298.15}^T H_m°$ (J·mol⁻¹)	$\Delta_f H_m°$ (J·mol⁻¹)	$\Delta_f G_m°$ (J·mol⁻¹)
a. liquid						
298.15	364.454	533.120	533.120	0	−1408000	−1036089
300	365.257	535.377	533.127	675	−1408128	−1033779
400	414.080	646.933	548.009	39570	−1414782	−907961
500	468.322	745.102	577.774	83664	−1419121	−780685
b. gaseous						
298.15	271.402	656.680	656.680	0	−1356000	−1020928
300	272.681	658.363	656.685	503	−1356300	−1018847
400	341.040	746.252	668.206	31218	−1371134	−904040
500	402.568	829.131	692.182	68474	−1382311	−785890
600	454.859	907.286	721.585	111420	−1389925	−665837
700	498.961	980.810	753.420	159173	−1394487	−544739
800	536.407	1049.948	786.208	210991	−1396525	−423183
900	568.414	1115.024	819.164	266273	−1396483	−301500
1000	595.884	1176.370	851.847	324523	−1394745	−179906
1100	619.516	1234.300	884.007	385322	−1391617	−58559
1200	639.884	1289.100	915.503	448317	−1387381	62440
1300	657.475	1341.030	946.256	513207	−1382234	183038
1400	672.703	1390.325	976.229	579734	−1376346	303225
1500	685.922	1437.198	1005.411	647681	−1369839	422987

$$\Phi_m° \stackrel{\text{def}}{=} \Delta_0^T S_m° - \Delta_{298.15}^T H_m°/T$$

The values: $a = 20.7540\cdot10^5$; $b = 589.1160\cdot10^{-3}$; and $c = 165.4624$, were calculated based on 92 points (193 K to 362 K). This equation has been used for an extrapolation of the thermodynamic functions up to 500 K.

Only two previous measurements on the heat capacity of TEOS are known. Ogier [5] measured the mean molar heat capacity in the temperature range 288 K to 371 K and Nkinamubanzi et al. [6] measured the heat capacity of TEOS at 298.15 K. The results differ by 1.3 and 3.5 per cent from those obtained in the present study.

Several papers on the standard enthalpy of formation of TEOS have been published in the literature. After recalculation of the measurements with recent auxiliary data (see reference 3), the results seem to split up in two groups: a) the combustion calorimetric determinations with values ranging from −1362 kJ·mol⁻¹ to −1385 kJ·mol⁻¹ [7,9–11], and b) the solution calorimetric determinations with values ranging from −1382 kJ·mol⁻¹ to −1422 kJ·mol⁻¹ [5,7,8]. To investigate this large range of 60 kJ·mol⁻¹ we have measured the enthalpy of formation of TEOS by means of solution calorimetry resulting in $\Delta_f H_m°(298.15$ K$) = -(1408.0 \pm 2.1)$ kJ·mol⁻¹ [3]. Since the nature of the amorphous silicon dioxide formed in previous determinations is an uncertain factor, we have avoided this problem in our thermodynamic cycle in such a way that no precipitation of silicon dioxide occurred. We have selected the value:

$$\Delta_f H_m°(Si(OC_2H_5)_4, 1, 298.15 \text{ K}) = -(1408.0 \pm 5.0) \text{ kJ·mol}^{-1}$$

From the heat capacity equation and the selected enthalpy of formation the thermodynamic functions of $Si(OC_2H_5)_4(l)$ can be calculated (Table I).

Table II. — Comparison of statistical and second-law entropies for $Si(OC_2H_5)_4$(g) and comparison of the enthalpies of vaporization by second-law and third-law evaluation of vapour pressure measurements.

reference	method[a]	T_{mean}/K	$S°(T)$/J·mol^{-1}·K^{-1}		$\Delta_v H°$(298.15 K)/kJ·mol^{-1}	
			Exp.	Calc.	2nd law	3rd law
Solana and Moles [15]	S	365.8	706.2	716.8	48.14	51.82
Reuther and Reichel [16]	S	308.1	674.2	665.8	54.53	51.83
Nadzhafov and Shaulov [10]	S	370.0	722.5	720.5	52.91	51.64
D'yachkova et al. [17]	M	313.0	627.6	670.1	35.24	48.36
Thomas et al. [18]	E	376.8	730.6	726.3	53.99	52.21
Kato and Tanaka [19]	E	421.0	761.7	764.0	50.71	51.68
Van der Vis et al. [4]	M	382.5	735.2	731.3	53.88	52.26

[a]E = ebulliometry; M = membrane null manometer; S = static.

4.   Thermodynamic functions of $Si(OC_2H_5)_4$(g).

The thermodynamic functions of gaseous TEOS (Table I) have been calculated from the molecular paramaters listed below, using a harmonic oscillator rigid rotor approach.

Moment of inertia: $I_{ABC} = 5.5345 \cdot 10^{-111}$ g^3·cm^6,

Symmetry number (S_4 symmetry): $\sigma = 2$,

Electronic energy levels: $g_0 = 1$ (ground state only),

Vibrational frequencies (degeneracy):

2985(8), 2981(4), 2938(4), 2897(4), 1489(4), 1462(4), 1447(4), 1394(4), 1374(4), 1304(4), 1176(4), 1115(1), 1090(1), 1089(2), 965(4), 936(4), 805(4), 794(3), 652(1), 478(4), 400(3), 311(2), 249(4), 200(1), 150(2), 100(1), 27(4), 13(4) cm^{-1},

The moment of inertia has been calculated from structural parameters [2], which have been estimated by comparison of isostructural compounds like tetramethoxysilane [12], ethanol, and methanol [13]. The symmetry of tetraethoxysilane has been taken the same as for tetramethoxysilane. Since Si^{4+} has a closed shell electronic structure a non-degenerated electronic ground state has been taken. The vibrational frequencies have been taken from our infrared and Raman study of gaseous TEOS, except the frequencies for SiOC deformation, CO torsion, and SiO torsion. The SiOC deformation modes, 200(1), 150(2), 100(1) cm^{-1}, have been assumed to be identical to the ab initio calculated frequencies for $Si(OCD_3)_4$ [14]. The torsional frequencies, 27 and 13 cm^{-1}, have been estimated by optimizing the agreement between second- and third-law evaluations of vapour pressure measurements [4,10,15–19] as summarized in Table II.

Though the agreement between second- and third-law enthalpies of vaporization, and second-law and statistical entropies is very good, one has to realize that uncertainties arising from the estimation of the structure, the estimation of the SiOC-deformation frequencies, and possibly the presence of a rotational barrier, all have been incorporated into the estimated values of the torsional frequencies.

A graphical representation of our vapour pressure measurements [4], using a Bourdon spoon gauge technique is given in Fig. 2. There is good agreement with other measurements, except the study by D'yachkova et al. [17]. Since the second- and third-law enthalpies of vaporization derived from the measurements of D'yachkova et al. also show a poor agreement, their results have been disregarded.

From the enthalpies of vaporization derived from the vapour pressure measurements (Table II), and calorimetric determinations by Ogier [5], $\Delta_{vap}H°_m$(438 K) = 40.5 kJ·mol^{-1}, and Voronkov et al. [11], $\Delta_{vap}H°_m$(298.15 K) = (48.5 ± 0.5) kJ·mol^{-1}, we have selected the value: $\Delta_{vap}H°_m$(298.15 K) = (52.0 ± 2.0) kJ·mol^{-1}. Combining this value with the standard molar enthalpy of formation of liquid TEOS results in:

$\Delta_f H°_m$($Si(OC_2H_5)_4$, g, 298.15 K) = −(1356.0 ± 6.0) kJ·mol^{-1}.
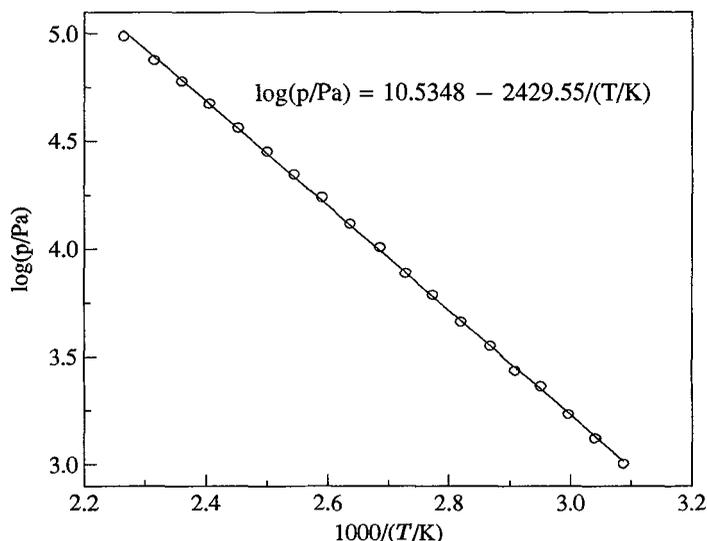
Fig. 2. — Vapour pressure of tetraethoxysilane from 323 to 441 K.

5. In-situ infrared study of the thermal decomposition.

The thermal decomposition of TEOS has been studied under the following conditions:

a) low-pressure (10^{-3} mbar argon) at 800 K
b) atmospheric pressure (argon atmosphere) at 800 K
c) atmospheric pressure (oxygen atmosphere) at 545 K.

The decomposition products have been identified according to the characteristical vibrational frequencies, summarized in Table III. The offset temperature of thermal decomposition of TEOS at low pressure is about 700 K. The pyrolysis has been studied at 800 K resulting in a reaction period of 3 hours. The decomposition products are ethene (mole fraction 0.43), ethanol (0.24), methane (0.14), carbon monoxide (0.11) , ethanal (0.07), and water (0.01) (Fig. 3.b). Visual inspection of the cell showed a white deposit which was identified by infrared spectroscopy and X-ray diffraction as amorphous silicon dioxide.

Compared with the reaction at low pressure there are only very small differences at atmospheric pressure (argon atmosphere). The same decomposition products are observed in almost the same relative abundances. The decomposition started at about 600 K which is 100 K lower than the low-pressure reaction. The time needed for complete pyrolyis at 800 K decreased to 1 hour.

The addition of oxygen instead of argon resulted in a lowering of the decomposition temperature to 450 K. The reaction has been studied at 550 K covering a reaction period of several hours. The products now formed are water, carbon dioxide, methanal, ethanal, and carbon monoxide (Fig. 3.c).

Table III. — Characteristic bands of several gaseous compounds involved in the decomposition process of tetraethoxysilane.

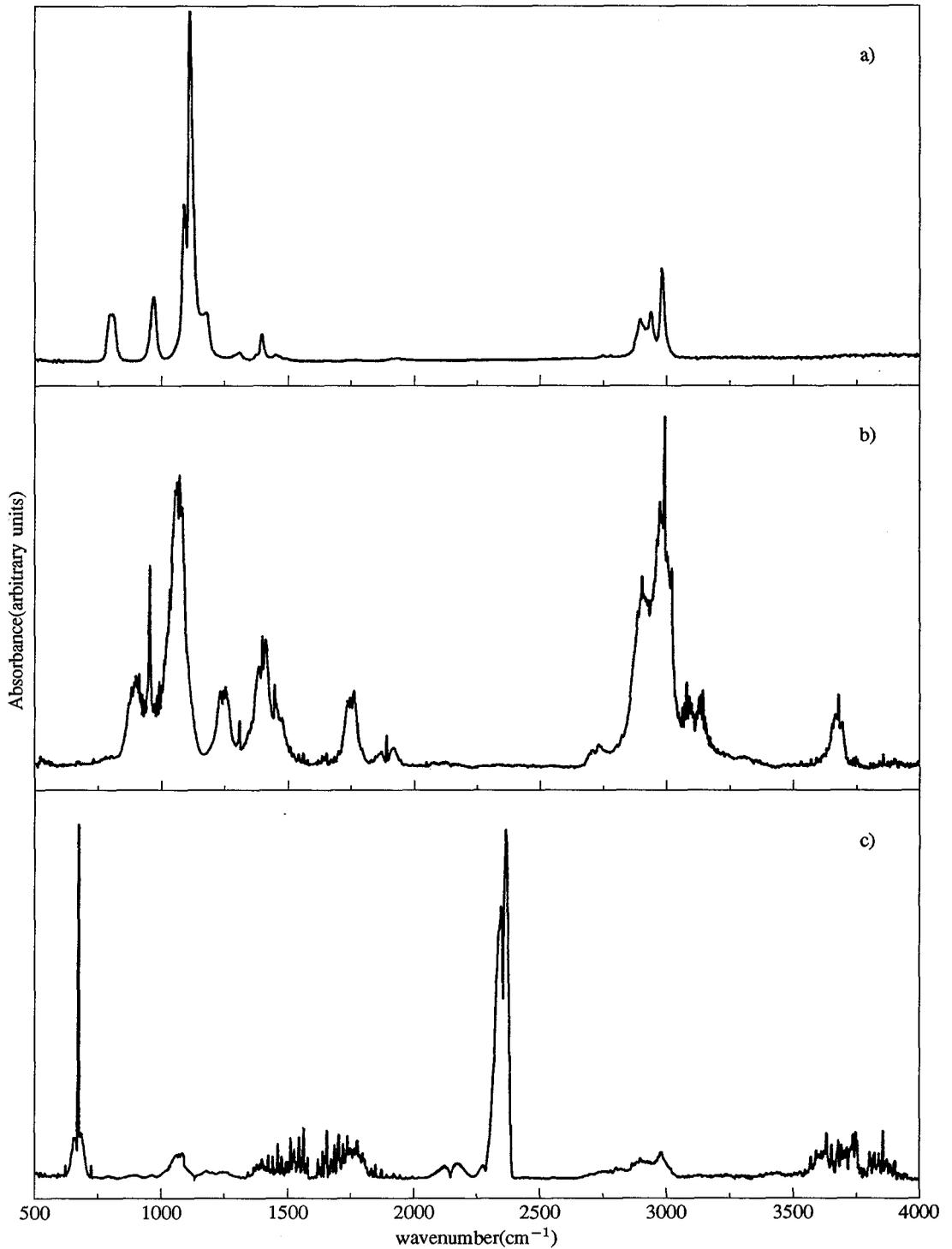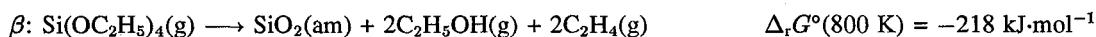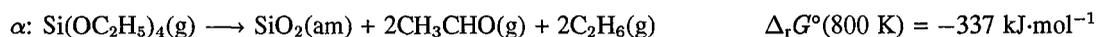| compound	wavenumber/cm^{-1}	compound	wavenumber/cm^{-1}
$Si(OC_2H_5)_4$	800(Si–O), 1115(C–O)	H_2CO	1776(C=O)
C_2H_5OH	1070(C–O), 3678(O–H)	CH_3CHO	1747(C=O)
C_2H_4	951(C=C), 2990(C–H)	CO	2145
CH_4	1308, 3020	CO_2	670 2350
H_2O	1400-1800, 3600-3800		

Fig. 3. — Infrared spectra of a) TEOS, b) product spectrum of pyrolysis at low pressure, and c) product spectrum of pyrolysis at atmospheric pressure in oxygen.

6. Discussion.

Several papers on the thermal decomposition of TEOS at atmospheric pressure have been published [20–22]. Heunisch [20] performed pyrolysis experiments in nitrogen atmosphere at 890 K and detected ethanol, ethanal, and possibly ethane and ethene. Ivanov *et al.* [21] performed a series of experiments in argon atmosphere in the temperature range 873 to 1273 K. At 873 K the products identified are silicon dioxide (mole fraction 0.18), ethanol (0.32), ethanal (0.16), ethene (0.31), water (0.02), and hexaethyldisilane (0.006). The presence of hexaethyldisiloxane was explained by the radical mechanism. Chu *et al.* [22] have made an kinetic study on the decomposition of TEOS in argon atmosphere (725 Torr) in the temperature range 721 K to 820 K.

Based on these studies three different mechanisms for the thermal decomposition of TEOS have been proposed [23], which can account for the observed decomposition products. The first mechanism is a radical chain reaction. The radical chain mechanism has been proposed to account for the pyrolysis of compounds like tetramethoxysilane which decompose in almost a similar way but are not able to form a intermediate ring-complex proposed in the other mechanisms. Mainly because of the low activation energy and the low pre-exponential A-factor in the Arhenius equation [22,24,25], the intramolecular reaction is believed to dominate for TEOS. For a radical mechanism one should expect the activation energy to be in the order of magnitude of the C-O (340 kJ·mol^{-1}) bond energy. The activation energy for tetramethoxysilane, 340 kJ·mol^{-1} [22], indeed suggests a radical mechanism. The activation energy for TEOS decomposition, about 200 kJ·mol^{-1} [22,24,25] is, however, considerably lower.
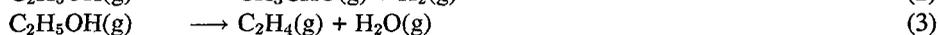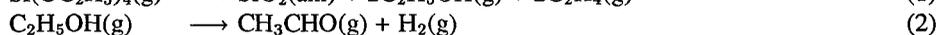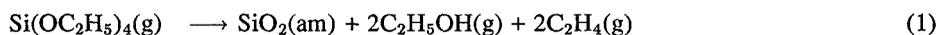
The other two mechanisms, α- and β-elimination, consist of an intramolecular reaction involving a intermediate ring-complex. α-Elimination, hydrogen abstraction from the CH_2 group, leads to the formation of ethanal and ethane while β-elimination, hydrogen abstraction from the CH_3 group, gives ethanol and ethene as principal decomposition products. Using the thermodynamic functions of TEOS the Gibbs energy of the two reactions at 800 K can be calculated (thermodynamic functions of the decomposition products were taken from ref. 13 and 26)

$$\alpha: \ Si(OC_2H_5)_4(g) \longrightarrow SiO_2(am) + 2CH_3CHO(g) + 2C_2H_6(g) \qquad \Delta_rG^\circ(800 \text{ K}) = -337 \text{ kJ·mol}^{-1}$$

$$\beta: \ Si(OC_2H_5)_4(g) \longrightarrow SiO_2(am) + 2C_2H_5OH(g) + 2C_2H_4(g) \qquad \Delta_rG^\circ(800 \text{ K}) = -218 \text{ kJ·mol}^{-1}$$

From these calculations it can be concluded that both α- and β-elimination are thermodynamically favourable. The experimental observations showed, however, that only a very small amount of ethane is formed during the reaction, implying that β-elimination predominates. A possible explanation for this observation is the fact that for β-elimination only minor rearrangements of the molecule are necessary, while for α-elimination a larger rearrangement is needed leading to a higher activation energy. The same effect is for example observed in the pyrolysis of diethylether [27]. Bearing in mind the estimated structure of TEOS [2] it can also be seen that the possibility of a CH_3 group to be near an oxygen of another ethoxy group is very small due to steric effects, which also explains that α-elimination does not occur.

A study by Delperier *et al.* [28] at low-pressure in a flow-reactor also showed equal amounts of ethanol and ethene. In our in-situ experiments the different amounts of ethanol and ethene can be explained by the pyrolysis of ethanol. Ethanol is known to decompose to ethanal and hydrogen at 830 K [27]. Ethanal decomposes further to methane and carbon monoxide.

Based on our observations the following reactions are proposed to occur successively during the decomposition of TEOS in inert atmosphere:

$$Si(OC_2H_5)_4(g) \longrightarrow SiO_2(am) + 2C_2H_5OH(g) + 2C_2H_4(g) \qquad (1)$$
$$C_2H_5OH(g) \longrightarrow CH_3CHO(g) + H_2(g) \qquad (2)$$
$$C_2H_5OH(g) \longrightarrow C_2H_4(g) + H_2O(g) \qquad (3)$$
$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g) \qquad (4)$$

The first reaction leads to the formation of silicon dioxide accompanied by the generation of ethanol and ethene. Pyrolysis of ethanol results in the formation of ethanal (2) and in a small amount of water (3). Thermal decomposition of ethanal produces equal amounts of methane and carbon monoxide (4). A consequence of the decomposition scheme given is that the amount of ethene should equal the sum of ethanol, ethanal, and methane as is observed in this study, and by Delperier *et al.* [28].

During the pyrolysis of TEOS in oxygen atmosphere only the organic compounds ethanal and methanal are observed. Other products like ethene, or ethanol are either not formed or easily consumed in the reaction process. Probably the initiating step is the formation of oxygen radicals followed by the formation of an oxygen-TEOS intermediate which decomposes to ethanal. This could probably explain the absence of any oxygen free organic compounds (e.g. ethene). Further oxidation of ethanal results in methanal and finally in the formation of carbon dioxide and water. The same reaction products have been observed by Kawahara *et al.* [29] who investigated the decomposition of TEOS in oxygen/ozone at temperatures ranging from 333 to 403 K. The formation of oxygen radicals has also been suggested by Pavalescu and Kleps [24], who have made a kinetic study of the decompostion of TEOS in an oxygen atmosphere. They reported the activation energy to be -26 kJ$\cdot$mol^{-1} which they considered to be associated with the adsorption-dissociation process of O_2 molecules.

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