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A detailed kinetic study of the thermal decomposition of tetraethoxysilane

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Abstract

This work presents a detailed kinetic modelling study of the thermal pyrolysis of tetraethoxysilane (TEOS). A chemical mechanism is proposed based on an analogy between the hydrocarbon branches attached to the central silicon atom and an existing mechanism for the decomposition and combustion of ethanol. Important reaction pathways are identified through element flux and sensitivity analyses. It was found that the key reaction routes are the step-wise four-centre molecular decomposition of TEOS to form silanols and ethylene: $\mathrm{Si(OH)}_n(\mathrm{OC_2H_5})_m \rightarrow \mathrm{Si(OH)}_{n+1}(\mathrm{OC_2H_5})_{m-1} + \mathrm{C_2H_4}$ $(n+m=4)$ and the barrier-less C$-$C bond cleavage of the ethoxy branches: $\mathrm{Si(OH)}_n(\mathrm{OC_2H_5})_m \rightarrow \mathrm{Si(OH)}_n(\mathrm{OC_2H_5})_{m-1}\mathrm{OCH_2} + \mathrm{CH_3}$ $(n+m \leq 4)$. Rate constants were calculated using conventional and variational transition state theories (TST and VTST) for all the reactions in the first route and for the methyl radical removal from $\mathrm{Si(OH)_3(OC_2H_5)}$ in the second route. The calculated results are similar to the rate constants of the corresponding ethanol reactions, providing support for the analogy with the ethanol decomposition. Simulations using the proposed mechanism are shown to be consistent with experimental data for the decomposition of TEOS.

Contents

1 Introduction

Tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$ is a widely used precursor for the synthesis of silicon dioxide nanoparticles. TEOS is a cheap, halide-free compound and enables cost-effective manufacture without toxic byproducts such as HCl gas [13]. Moreover, SiO_2 films prepared from TEOS in chemical vapour deposition reactors have gained significance for their application in microelectronic devices, where such films offer better performance than alternatives manufactured from silane (SiH_4) [1, 5].

The industrial importance of TEOS-based processes and an increasing desire to tune the properties of the nanoparticulate product motivate the need to understand the kinetics of the thermal decomposition of TEOS. A detailed mechanism describing this chemistry would provide valuable insight into how to control the product characteristics.

There have been a number of studies to investigate TEOS chemistry. Delperier et al. [7] investigated the thermal behavior of TEOS in a chemical vapour deposition reactor. The main reaction products were shown to be ethylene and ethanol. The authors proposed a model to describe the measured global conversion and developed an understanding of the main process parameters influencing the conversion. However, the model assumed simple quasi-molecular processes and no consideration was given to possible routes for TEOS decomposition.

Chu et al. [4] performed experiments in a heated wall reactor to compare the thermal stabilities of TEOS and tetramethyl orthosilicate (TMOS). They found that TEOS is significantly less stable than TMOS and proposed an initial decomposition model for both compounds. In case of TEOS, they suggested an initiating six-center decomposition reaction leading to the formation of diethoxy silicate $(C_2H_5O)_2Si{=}O$ and equal amounts of ethanol and ethylene.

Ho and Melius [12] subsequently performed a computational study to estimate the thermodynamic data for a number of silica species believed to be important in the thermal decomposition of TEOS. Shock tube experiments by Herzler et al. [11] confirmed the main decomposition products as ethylene and ethanol. However, the products were observed to appear (approximately) in a 4:1 ratio, which was noted to be inconsistent with the model used by Chu et al. [4]. Herzler et al. [11] performed a further mechanistic analysis and suggested the 1,2-elimination of ethylene as the most likely alternative. They proposed a kinetic model for the decomposition of TEOS, where the model parameters were fitted against their observations. It should be noted that they were unable to detect any silica intermediates, and reported a number of difficulties in modelling the formation of ethanol. In particular, it was noted that one of the model variants required the specification of an energy barrier for the ethanol reactions that contradicted the thermodynamic data from Ho and Melius [12]. These problems led the authors to propose two chemical mechanisms, one with and one without the formation of ethanol included. Although an ethanol producing reaction is included in the current model as suggested by Coltrin et al. [5] , the results show that there must be another reaction playing an important role in the formation of ethanol. This is a subject of ongoing investigation.

Kraft and co-workers [20, 25–27] recently initiated an investigation of TEOS decomposition, using computational chemistry methods to work around the difficulties of observing silica intermediates. Thermodynamic data were calculated for all species [20], and equilibrium calculations used to identify the most stable species [26]. Key reaction steps were proposed based on the species identified by the equilibrium calculations, and a heuristic model developed where TEOS undergoes step-wise decomposition to form silicic acid $Si(OH)_4$. Although the model reproduces Herzler's experimental results [11] and is thermodynamically consistent, it is considered to be incomplete in the sense that it contains heuristic reactions with fitted parameters, and does not necessarily consider all possible reaction pathways.

The purpose of the current work is to develop a comprehensive mechanism to describe the thermal decomposition of TEOS. This paper aims to: (i) present a systematic analysis of possible reaction pathways, (ii) identify the most plausible species and reactions, (iii) calculate, for a first time, rate constants for key reactions using transition state (TST) and variational transition state (VTST) theory, and (iv) critically assess the proposed model against experimental data.

2 Computational details

In order to build a detailed mechanism of the TEOS pyrolysis plausible elementary steps have to be identified. As discussed previously, the scope of the literature is relatively narrow, as only the most important reactions and species are discussed. Manual derivation of the detailed model combined with the ab initio calculations of the rate constants is computationally intractable. Therefore, it was decided to use an automated approach where the mechanism is systematically created according to the rules taken from a similar kinetic system. Then, an initial mechanism can be built with reasonably assigned rates constants as a starting point for further investigation.

In this work, an automatic method to identify possible reaction pathways for the thermal decomposition of TEOS was developed by drawing an analogy between the decomposition of ethanol and the decomposition of the ethoxy branches in silica species. Ethanol is considered to be a good candidate for this task because, as it will be shown in the next sections, there are number of similarities between both systems.

2.1 Kinetic model generation

The ethanol decomposition reactions in the mechanisms proposed by Marinov [17] and Park et al. [19] were used to propose a set of rules to describe the decomposition of the $-OC_nH_m$ groups in TEOS. The rules were recursively applied to systematically suggest all permutations of species and reactions that could participate in the decomposition. In each case, initial estimates of the reaction rate parameters were taken from the corresponding ethanol reaction in the Marinov mechanism, unless stated otherwise. This procedure also identified a large number of species that are non-physical or extremely short-lived. In order to avoid such problems, a termination criterion was introduced such that species with more than one radical site were rejected on the grounds that they were considered to be too unstable. The rules used to generate the TEOS decomposition mechanism de-

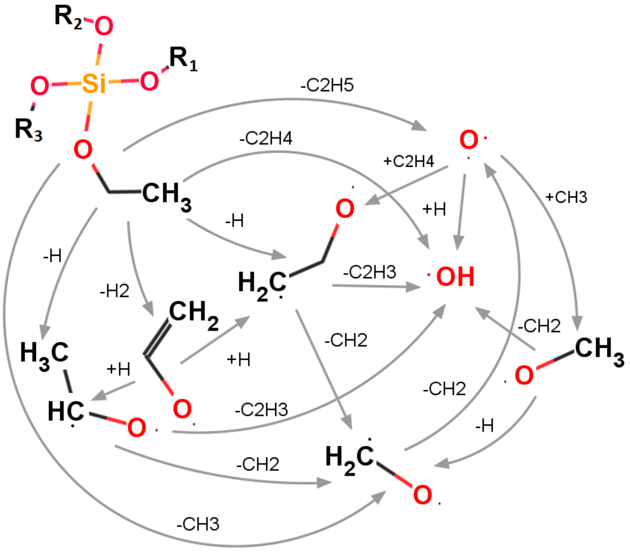


Figure 1: *Mechanism generation steps.*

scribed in this work are summarised below. Note that the proposed reactions channels are all considered to be reversible, such that some care is required to avoid double counting.

a) Reactions for $-OC_2H_5$ branch

Allowed reactions are the 1,2-elimination of ethylene, $C-C$ and $O-C$ bond fission, hydrogen abstraction of primary and secondary hydrogens and $C{=}C$ bond formation. Additionally, the TEOS hydration pathway proposed by Coltrin et al. [5] was included, were the ethoxy branch attached to TEOS and the subsequent silica species react with water to form ethanol. The first reaction is suggested by Herzler et al. [11] as the main initiating channel of the TEOS decomposition and the main source of the detected ethylene. The second reactions occur in parallel with ethylene release and produce radicals that result in subsequent chain processes. Initial estimates of the rate parameters for the $C{=}C$ bond formation reactions were taken from Park et al. [19].

b) Reactions for $-OCH_3$ and $-OCH_2$ branches

Allowed reactions are hydrogen abstractions converting one branch into another $-OCH_2 + H-X \longleftrightarrow -OCH_3 + X$, where $H-X = \{H_2O, H_2, OH, CH_4, H_2O_2\}$ and methylene radical (CH_2) removal from methyl and methylene groups: $-OCH_3 \longleftrightarrow -OH + CH_2$, and $-OCH_2 + H \longleftrightarrow -O + CH_3$.

c) Reactions for $-OCH{=}CH_2$ branch

Allowed reactions are direct hydrogen additions to the two carbon centers of the double bond: $-OCH{=}CH_2 + H \longleftrightarrow -OCH_2CH_2$ and $-OCH{=}CH_2 + H \longleftrightarrow -OCHCH_3$ with rates taken from the computational study of Rao et al. [23].

d) Reactions for $-O$ and $-OH$ branches

Allowed reactions are methyl and ethyl radical $-O + CH_3/C_2H_4 \longleftrightarrow -OCH_3/-OC_2H_4$ and hydrogen additions $-O + H-R \longleftrightarrow -OH + R$ to the $-O$ group.

e) Reactions for $-OC_2H_4$ and $-OCHCH_3$ branches

As the hydrogen additions to the radical sites are already included in the $-OC_2H_5$ reaction list, the remaining allowed channels are CH_2 and C_2H_3 radical removal.

The described TEOS decomposition rules are schematically presented on Figure 1. Any combination of the depicted hydrocarbon branches are allowed to be attached to the central silica atom, provided that the total number of radical sites is no greater than one.

2.2 Flux and sensitivity analyses

Flux and sensitivity analyses were used to identify key reaction pathways and species in the underlying chemical mechanism. Fluxes and sensitivities are time-resolved quantities. In case of the flux analysis an integration was performed summing up the net flow of atomic silicon. In case of sensitivity analysis the maximum sensitivity coefficients were taken as an importance indicator of a given parameter.

The integrated flux of element i between species j and k through reaction r is defined as:

$$F_{r,j,k} = V_r \int_0^t \frac{n_{i,j} n_{i,k} r_r(t)}{N_{i,r}} \mathrm{d}t \quad [\mathrm{mol}] \tag{1}$$

where V_r is the volume of the reacting mixture, $n_{i,j}$, and $n_{i,k}$ are the numbers of element i in species j and k respectively. The rate of the reaction is given by r_r and the sum of the atoms of element i on either side of the reaction r is $N_{i,r}$.

The maximum normalised sensitivity coefficient is defined as:

$$S_{i,k} = \max_t \left\{ \frac{A_i}{X_k(t)} \left(\frac{\partial X_k(t)}{\partial A_i} \right) \right\} \tag{2}$$

where A_i is the vector of model parameters and $X_k(t)$ is the dependent variable chosen as a measure of sensitivity. In this work, the pre-exponential factors of each reaction in the mechanism were taken as model parameters and concentration of silicic acid $Si(OH)_4$ was used to calculate model response.

2.3 Rate estimation

Geometries of reactants, products and transition states were calculated via Gaussian 09 [8] program suite using the B97-1 hybrid functional [2] and 6-311+G(d,p) basis set. The chosen functional is deemed as being the best choice for DFT calculations giving compromise between accuracy and computational time [3].

The reaction rates coefficients for the most important channels with barriers were estimated via conventional transition state theory (TST) using the Polyrate [28] software package. The partition functions were calculated by applying the rigid rotor harmonic oscillator treatment (RRHO). In cases where there existed multiple reacting routes an appropriate degeneracy factor was applied.

The rates of the most important barrier-less reactions were estimated via RRKM (Rice-Ramsperger-Kassel-Markus) [14, 18, 24] theory implemented in the Unimol [10] code using a simple Gorin Model [21]. The Gorin model approximates the internal modes of motion of the transition state structures as being given by the vibrations and rotations of the separated fragments of the product. It is also assumed that the geometries of these radical fragments do not change along the reaction path (except interfragment separation) and that the low frequency bending modes associated with the breaking bond are considered to be 1-dimensional and 2-dimensional rotations. Given that the identified transition states occurred at relatively large separations it was decided to model these rotational motions using free rotor treatments. The rotational constants were found by the Pitzer formula [22] (torsional motion) and the Unimol package (remaining parameters). The potential energy as a function of interfragment separation was approximated by a Morse potential,

$$E(r) = D_e\left[1 - \exp\{-\beta(r - r_{\mathrm{eq}})\}\right]^2 \quad [\mathrm{kJ/mol}] \tag{3}$$

where D_e is the bond dissociation energy, r is the reaction coordinate, r_{eq} is the value of r at equilibrium, and β describes the steepness of the potential function,

$$\beta = \left(\frac{2\pi^2\mu}{D_e}\right)^{\frac{1}{2}} \nu \quad \left[\mathring{\mathrm{A}}^{-1}\right] \tag{4}$$

where μ is the reduced mass of the bonded fragments and ν is the vibrational frequency of the breaking bond.

The Gorin model was applied to estimate the rate constants of barrier-less reactions. The method is typically accurate to within a factor of 2-5 [9]. However, it is known to be sensitive to the accuracy of the estimated reactant energies. The G2 composite method was used to calculate these energies [6] in order to increase the accuracy as compared to simple DFT calculations. This technique combines the results of several quantum chemistry calculations performed at different levels of theory and basis sets to correct final energies. As G2 computations quickly become too expensive with increasing size of the molecular system, it was decided to perform these calculations on only one barrier-less reaction involving smallest silica species. A C$-$C bond fission in triol: $\mathrm{Si(OH)_3(OC_2H_5)} \longleftrightarrow \mathrm{Si(OH)_3(OCH_2)} + \mathrm{CH_3}$ was deemed as the most appropriate choice, because it involves the smallest silica compound. This choice minimises the computational effort and is expected to maximise the accuracy of the quantum calculations. Outcomes from the following computations were applied to other related channels.

3 Results

3.1 Gas-phase mechanism

A detailed gas-phase mechanism of TEOS thermal decomposition was compiled using the strategies described in section 2.1. The mechanism contains 115 silica species taking part in 1660 reactions. Additionally, the carbon C_2 combustion chemistry proposed by Marinov [17] was added to the mechanism in order to provide reaction pathways for

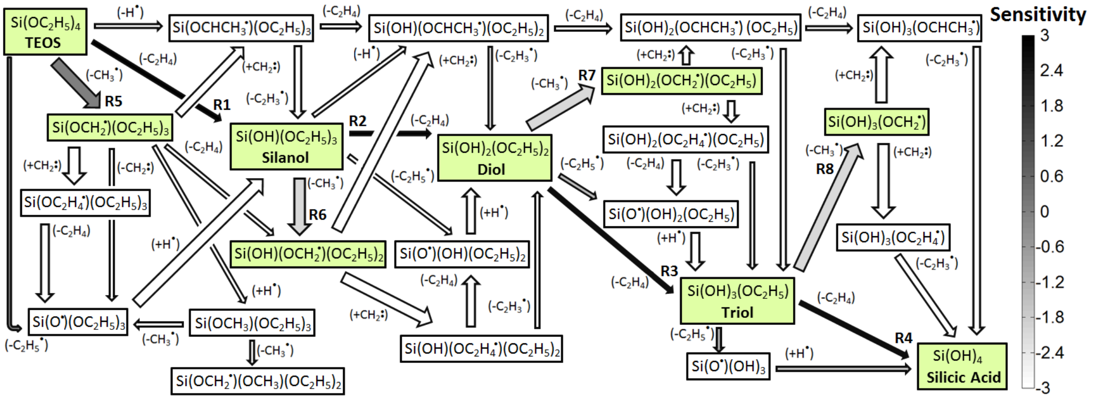


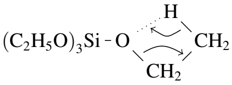
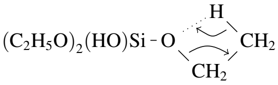
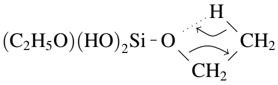
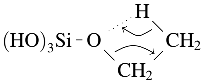
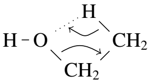
Figure 2: *Integrated fluxes of Si and the most sensitive channels during the decomposition of TEOS. Thickness and color of each arrow indicate how many moles of the atomic silica were exchanged between pair of species and how sensitive given reaction is with respect to the concentration of $Si(OH)_4$.*

the various hydrocarbon species created during the process. It is believed that the chosen reaction and species pool was large enough to capture the most important processes, and it is expected that it will be possible to later remove some of this pool without compromising the model. Flux and sensitivity analyses were used to identify the most important species and reactions.

3.2 Important reaction pathways and species

The outcomes from the flux and sensitivity analyses are depicted on Figure 2. The calculations were performed with an initial concentration of 0.5% TEOS in Ar at 1500 K and 1 bara, and simulated for a reaction time of 0.1 ms. Each node on the plot corresponds to a species with a significant flux. The thicknesses of the arrows is proportional to the flux of Si between a pair of species. The colors of the arrows depict the sensitivity. Each computed sensitivity coefficient was assigned an appropriate tint from a logarithmic grayscale placed on the right side of the plot. Additionally, compounds deemed as being very important are highlighted by using coloured labels.

Figure 2 shows that the decomposition proceeds via a complex network of reactions. However, the main TEOS decomposition pathway is clearly seen. It is either direct (ethylene elimination R1-R4) or indirect formation of silanols: silanol $Si(OH)(OC_2H_5)_3$, diol $Si(OH)_2(OC_2H_5)_2$, triol $Si(OH)_3(OC_2H_5)$ and silicic acid $Si(OH)_4$ (various routes where the most important are C−C bond fission R5-R8, and hydrogen and methylene radical additions). The main product is silicic acid. This finding is in agreement with the equilibrium calculations of Phadungsukanan et al. [20] where it was found that $Si(OH)_4$ is one of the most prevalent silica species over a wide range of the temperatures. Moreover, silanols and silica compounds created following C−C bond fission have the largest Si flux indicating their importance for the whole decomposition process. This is consistent with the sensitivity analysis where channels leading to their formation (R1-R8) were found to have the biggest impact on the model response.

	Reactions	$\triangle H_r^0$ (0 K)	$\triangle H^{\ddagger 0}$ (0 K)	k_∞ (500-1800 K)
R1	 $(C_2H_5O)_3Si-O\overset{H}{\underset{CH_2}{\frown}}CH_2$	51.05	248.32	$7.896\times10^{13}T^{-0.139}\exp(-261.46/RT)$
R2	 $(C_2H_5O)_2(HO)Si-O\overset{H}{\underset{CH_2}{\frown}}CH_2$	51.25	248.07	$7.896\times10^{13}T^{-0.215}\exp(-260.99/RT)$
R3	 $(C_2H_5O)(HO)_2Si-O\overset{H}{\underset{CH_2}{\frown}}CH_2$	52.59	247.65	$7.896\times10^{13}T^{-0.534}\exp(-265.14/RT)$
R4	 $(HO)_3Si-O\overset{H}{\underset{CH_2}{\frown}}CH_2$	50.71	246.35	$7.896\times10^{13}T^{0.015}\exp(-257.02/RT)$
R8	$(HO)_3SiOCH_2\cdots CH_3$	370.03[a]		$4.680\times10^{18}T^{0.081}\exp(-377.98/RT)$
Et1	 $H-O\overset{H}{\underset{CH_2}{\frown}}CH_2$	50.04	262.34	$7.896\times10^{13}T^{0.011}\exp(-273.00/RT)$
Et2	$HOCH_2\cdots CH_3$	361.87[a]		$3.030\times10^{17}T^{0.363}\exp(-368.61/RT)$

[a] Obtained from Gaussian G2 composite method

Table 1: *Standard reaction $\triangle H_r^0$ and activation $\triangle H^{\ddagger 0}$ enthalpies (kJ/mol), and high pressure rate constants (s^{-1}) for selected silica reactions and their ethanol analogues. All quantum calculations were performed at B971/6-311+G(d,p) level of theory, unless stated otherwise.*

Note, however, that the TEOS mechanism was built based on the analogy with ethanol thermal pyrolysis where in the work of Marinov [17] or Li et al. [15, 16] the same reactions were revealed to be important. Thus, it is essential to check if our finding descends from applying ethanol kinetics or if it is also a feature of the TEOS system. One way to achieve this is to examine whether or not true rate constants for the key channels in silica differ from those in ethanol.

3.3 Rate constants for the selected channels

Table 1 summarizes the results of the ab initio rate constants calculations for the most important channels in the TEOS decomposition and the analogous ethanol reactions. The standard reaction and activation enthalpies (for reactions with barriers) at 0 K are presented along with high pressure rate constants fitted to a modified Arrhenius expression. It should be noted that the barrier-less reaction enthalpy explicitly evaluates the C-C bond dissociation energy which allows for direct comparison between ethanol and silica systems in terms of this quantity.

Table 1 shows that the activation barriers and reaction enthalpies are very similar between the silica R1-R4 channels having 2.1 kJ/mol of maximum difference. Further, each replacement of an $-OC_2H_5$ by an $-OH$ group results in decreasing of the barrier height by 0.42-1.26 kJ/mol. The analogous ethanol reaction Et1 was found to have slightly higher barrier 12.5-16.7 kJ/mol, but having a lower reaction enthalpy. In case of the barrier-less dissociation reactions, a Gaussian G2 composite method was used to more accurately describe their energetics. The calculated reaction enthalpies for channels R8 and Et2 are within 8.4 kJ/mol difference.

The data in Table 1 are consistent with other data for these reactions, where available in the literature. Ho and Melius [12] estimated reaction enthalpies at 0K for Et1 and R4 channels to be 50.2 kJ/mol and 48.53 kJ/mol respectively. This agrees well with our results. However, their activation barriers are as much as 41.84 kJ/mol and 25.1 kJ/mol higher. Ho and Melius stated that the uncertainty in their calculations is within 12-38 kJ/mol and note that their values are too high. It is likely that these discrepancies probably arise from Ho and Melius using a lower level of theory for the transition state species. Marinov [17] calculated the activation barrier of ethanol decomposition as 271.54 kJ/mol, which is in good agreement with our results. Further, Marinov's critical energy of C−C bond fission in ethanol compares very well with our calculations being only 0.88 kJ/mol higher.

Figure 3 compares the rate constants calculated in this work with the literature data for silicon and ethanol. The plots a) and b) depict silica reactions along with the results from experimentally derived rates of Herzler et al. [11]. Note, that Herzler's rates only slightly differ between R1-R4 and R5-R8 channels in their mechanism, thus only one value for ethylene and methyl radical removal is presented. The plots c) and d) show the calculated ethanol decomposition rate constants compared with the various modelling and experimental literature studies.

It can be seen from Figure 3a that the step-wise TEOS de-ethylation rates span all the values represented by Herzler's equivalent single-rate equation. The kinetics of Herzler's reaction were estimated by a global fit to the measured yield of the ethylene released during the process. Further, Herzler stated that a good fit was only obtained when the TEOS decomposition rate was made somewhat smaller than the other channels. This is consistent with the results presented here, where the elimination of ethylene from TEOS has one of the lowest rate. In case of the barrier-less C−C bond fission in triol presented on Figure 3b, again a good agreement with the Herzler's rates was obtained. Only small differences can be noticed which slowly increase with the temperature.

Figures 3c and 3d are presented for comparison to assess the accuracy of the computations and the suitability of using an ethanol mechanism as a starting point to describe the decomposition of TEOS. The obtained rates are consistent with the corresponding silanes channels providing an evidence that the similarity exist between both systems. Current methods are very good for barriered reactions whereas, as can be seen from Figure 3d, there is still room for improvement in case of reactions without clearly defined transition states. It is therefore suggested that use of a method more detailed than a simple Gorin model may be an essential next step in order to determine accurate values of these rate parameters.

3.4 Model prediction

Figure 4 shows yields of ethylene released as a fraction of consumed TEOS predicted by our model and experimentally measured by Herzler et al. [11]. Calculations were performed using a series of constant temperature batch reactor simulations, where each simulation temperature was taken from the results reported by Herzler. The initial con-

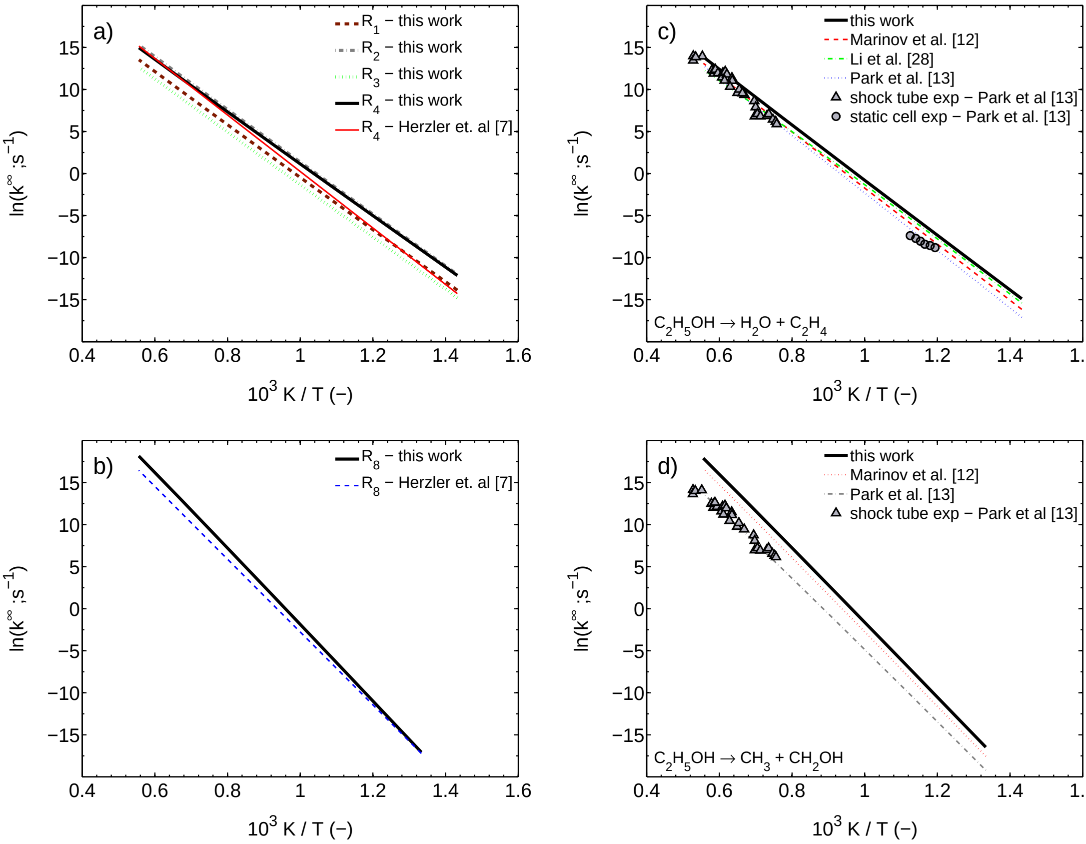


Figure 3: *Arrhenius plots of the rate constants for the step-wise de-ethylation and C−C bond fission reactions in most important silica species a), b) and ethanol c), d).*

centration of reactants was 420 ppm TEOS in Ar at the pressure 2 bara for the reaction time 500 μs.

It can be seen that a very good agreement with the experimental data was obtained for the temperatures above 1220 K, whereas below this value our results somewhat underestimate (15%-20%) the ethylene production. A potential explanation for the discrepancy is the fact that rate of ethylene production at these conditions was found to be sensitive to the uncertainty in the rate coefficients of the various reaction channels at these lower temperatures. The use of a more detailed calculation to better predict the rate constants for the barrier-less reactions may help resolve this issue. Taking this into account and the fact that no fitting was performed it can be stated that a current model is a good starting point for the derivation of the detailed TEOS gas-phase mechanism.

4 Conclusions

A comprehensive kinetic model of the thermal decomposition of TEOS was created using an automatic mechanism generation technique where possible reactions and species were systematically derived based on the analogy between ethanol combustion chemistry and

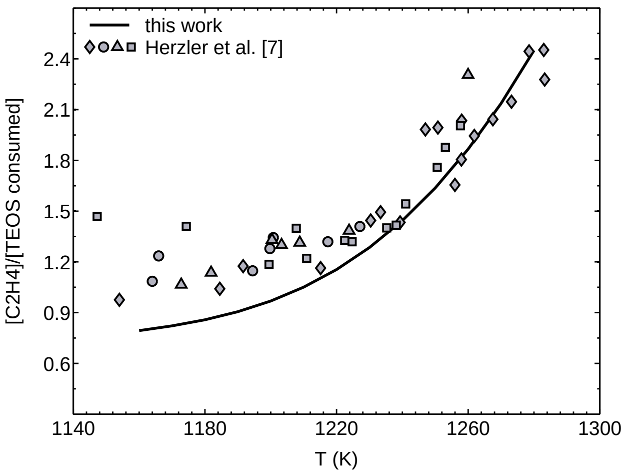


Figure 4: *Yields of ethylene as a fraction of consumed TEOS over the temperature range 1140-1300 K and pressure 2 bara. Solid line represents our modelling results compared to experimental measurements of Herzler et al. [11].*

hydrocarbon branches attached to silicon atom. The dominant decomposition pathways and compounds were identified by flux and sensitivity studies to be 1,2-elimination of ethylene and C−C bond scission leading to the formation of silanols and producing silicic acid $Si(OH)_4$ as the main stable product. Theoretical investigation of the rate constants for mentioned channels showed that a strong similarity exist between silica and ethanol systems. Finally, the model was tested against experimental measurements of Herzler et al. [11] and very good agreement was obtained.

Although, the current study is a step forward in the effort to derive complete kinetic model of the TEOS pyrolysis, more work is still required. For example, it would be very interesting to calculate rate constants for other channels and check how they compare with ethanol. Additionally, a more accurate method than simple Gorin Model might be necessary to properly describe barrier-less reactions.

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