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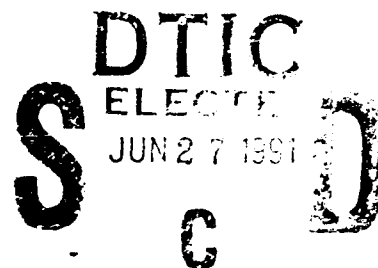
Relative Stabilities of Tetramethyl Orthosilicate

and Tetraethyl Orthosilicate in the Gas Phase

by

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$$k (\text{TMOS}) = 1.4 \times 10^{16} \exp (-81{,}200/RT) \ s^{-1}$$

$$k (\text{TEOS}) = 7.4 \times 10^{10} \exp (-49{,}500/RT) \ s^{-1}.$$

TMOS is significantly more stable than TEOS. The mechanistic implication of these results is discussed.

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and Tetraethyl Orthosilicate in the Gas Phase

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Abstract

The stabilities of $Si(OCH_3)_4$ and $Si(OC_2H_5)_4$ have been studied pyrolytically using highly diluted mixtures near atmospheric pressure conditions. FTIR spectrometric analyses of the disappearance of the reactants and the formation of various major stable products allow us to qualitatively account for the global difference in the measured overall first-order decay constants:

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TMOS is significantly more stable than TEOS. The mechanistic implication of these results is discussed.

1. Introduction

The deposition of SiO_2 as an insulating film is an important part of microelectronic fabrication process [1]. For the SiO_2 film preparation, there have been attempts to replace the traditional dry oxidation and silane oxidation processes by silicon alkoxide CVD (chemical vapor deposition) [2,3]. Despite the growing interest in this OMCVD (organometallic CVD) process, the kinetics and mechanisms of the thermal decomposition of silicon alkoxides or tetra-alkyl orthosilicates, $Si(OR)_4$, in the gas phase remain virtually unknown.

Because of the close coupling of the gas phase chemistry with surface reactions under normal atmospheric OMCVD conditions [4,5], it is of great importance that the kinetics as well as mechanisms of gas phase reactions be fully elucidated. For tetra-alkyl orthosilicates, the only gas-phase kinetic study, to our knowledge, was performed by Ivanov et al. [6] for tetraethyl orthosilicate, TEOS. The effective rate constant measured by a flow technique was reported to be $k \approx 10^6 \exp(-20,000/RT)$ s^{-1}, where R = 1.987 cal/mol.deg.

In order to compare the thermal stabilities of tetramethyl orthosilicate, TMOS, and TEOS, we have recently carried out a series of experiments using highly diluted mixtures of these compounds near atmospheric - pressure conditions to minimize surface effects. The products of the decomposition reactions were analyzed by Fourier-Transform Infrared (FTIR) spectrometry. The results of this pyrolytic study indicates that TMOS is far more stable than TEOS. This preliminary result will be discussed in terms of their reaction mechanisms.

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2. Experimental

The thermal decompositions of TMOS and TEOS were carried out in a 270 - ml quartz reactor heated with a double-walled cylindrical furance. The reactor temperature was controlled and measured to ± 0.5 K with a thermocouple placed in a small tube sealed at the center of the reactor employing a solid-state temperature controller (Omega CN-9000). The concentrations of the reactants were varied from 0.6 - 1.4% for TMOS and 0.06 - 0.30% for TEOS using argon as diluent. Pyrolysis was carried out between 858 and 968 K for TMOS and between 721 and 820 K for TEOS, providing a reasonable reaction period covering from several minutes to several hours. The reaction pressures for both systems were kept constant and maintained near atmospheric pressure to minimize reactor wall effects, which often alter not only the kinetics but also the mechanism of the initial, rate-controlling step.

Both pyrolyzed and unpyrolyze samples were analyzed by FTIR spectrometry with a Mattson Instrument Polaris spectrometer using a 15 cm long, 2.5 cm O.D. sample cell sealed with two KCl windows. The analysis cell was connected directly to reactor and the associated vacuum system, which could be evacuated to typically 5×10^{-5} torr before each run.

The reaction products identified in the TMOS decomposition by FTIR were CO, CH_2O, CH_3OH and CH_4. A typical set of spectra for the pyrolyzed and unpyrolyzed samples of TMOS, is shown in Fig. 1. A similar set of results for TEOS is presented in Fig. 2. As indicated in the figure, the decomposition products identified in this system are: CO, C_2H_4, CH_3CHO and C_2H_5OH.

The concentrations of the major products identified in the thermal decomposition reactions were calibrated with more than 10 sets of mixtures composing of varying amounts of products. The pressures of the calibration

samples were always kept the same as those of the expanded, pyrolyzed or unpyrolyzed reaction mixtures, in the absorption cell. In this manner, the effect of pressure (or Lorentz) broadening can be properly corrected for. The concentrations of reactants and products were quantitatively analyzed with a multicomponent analysis program supplied by Mattson.

3. Results

Typical sets of concentration-time profiles measured for the TMOS and TEOS systems are presented in Figs. 3 and 4, respectively. The rates of disappearance of both compounds were, unexpectedly, found to be approximately first order as illustrated in Fig. 5. From the slopes of these first-order plots one can evaluated the apparent first-order rate constants for the disappearance of the two reactants:

$$Si(OCH_3)_4 \quad \xrightarrow{k_1} \quad products \tag{1}$$

$$Si(OC_2H_5)_4 \quad \xrightarrow{k_2} \quad products \tag{2}$$

It should be mentioned that because of the formation of small molecular products, such as CO, CH_2O and CH_4, it is expected that both reactants may have been consumed, at least in part, by radical attacks, as will be discussed later.

The rate constants presented in Fig. 6 can be effectively represented by

$$k_1 = 1.4 \times 10^{16} \exp(-81,200/RT) \; s^{-1}$$

$$k_2 = 7.4 \times 10^{10} \exp(-49,500/RT) \; s^{-1}$$

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As is evident from above equations, the difference between these two systems in terms of both pre-exponential factor and activation energy is very significant. Overall, TMOS is significantly more stable thermally than TEOS. At 770 K, for example, k_1 is 4 orders of magnitude smaller than k_2.

Inasmuch as the difference in the strengths of Si-O and O-C bonds in these two molecules is not expected to be large, the observed dramatic difference in stabilities must have resulted from the intrinsic mechanistic variance between these decomposition processes.
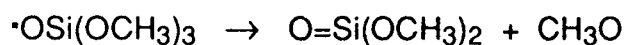
4. Discussion

The significantly different Arrhenius parameters measured for the thermal decomposition of TMOS and TEOS suggest that the rate-controlling steps in these two systems are greatly different. For TMOS, $A = 1.4 \times 10^{16}$ s^{-1} reflects a very loose transition state, typical for a bond-breaking process producing radical products. The high activation energy, 81 kcal/mole is qualitatively in accord with such a bond-breaking process. Although the strengths of the C-O and Si-O bonds in TMOS are not known, the former is likely to be in the range of 80 - 85 kcal/mole, while the latter $\geq$ 100 kcal/mole [7].

Thus, the initial decomposition of TMOS is most likely

$$Si(OCH_3)_4 \rightarrow \cdot CH_3 + \cdot OSi(OCH_3)_3$$

followed by a relatively short chain reactions. For example:

$$\cdot OSi(OCH_3)_3 \rightarrow O{=}Si(OCH_3)_2 + CH_3O$$
$$O{=}Si(OCH_3)_2 \rightarrow CH_3 + SiO_2 + CH_3O$$

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The $O=Si(OCH_3)_2$ molecule is expected to be a key intermediate because its carbon analog, $O=C(OCH_3)_2$, (dimethyl carbonate) is a very stable, commercially available chemical.

The production of CH_3O and CH_3 can account for the observation of CH_4, CH_2O and CO:

$$CH_3 + CH_3O \rightarrow CH_4 + CH_2O$$

$$CH_3 + CH_2O \rightarrow CH_4 + HCO$$

$$HCO + M \rightarrow H + CO + M$$
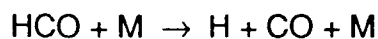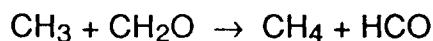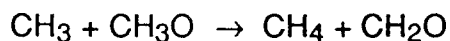
These radicals may also attack the parent TMOS molecule leading to the lowering of the activation energy. These subsequent radical reactions may in fact be unimportant; otherwise, TMOS decay would not obey the first-order rate-law and the A-factor for k_1 would be significantly lower-than 10^{16} s^{-1}. We hope to perform a rudimentary kinetic modeling to sort out the unimolecular decomposition kinetics in the near future.

Contrary to TMOS, the low A-factor and activation energy measured for TEOS suggest that the initial decomposition may occur by a rather tight, ring-complex, such as [6]

$$\rightarrow O=Si(OC_2H_5)_2 + C_2H_4 + C_2H_5OH,$$
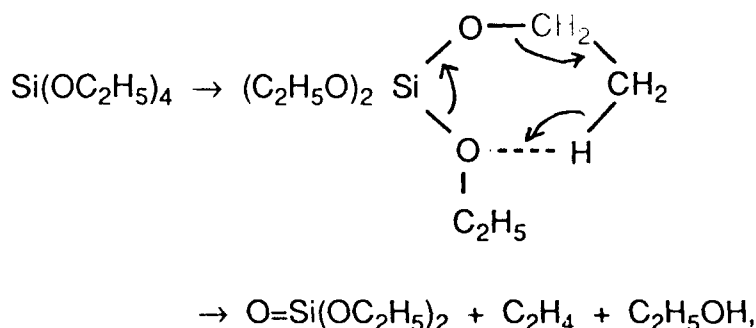
producing the stable molecular products as given. This mechanism is similar to the known 6-centered molecular decomposition process for the diethyl carbonate [8]:

$$O=C(OC_2H_5)_2 \rightarrow$$

$$\rightarrow CO_2 + C_2H_4 + C_2H_5OH,$$
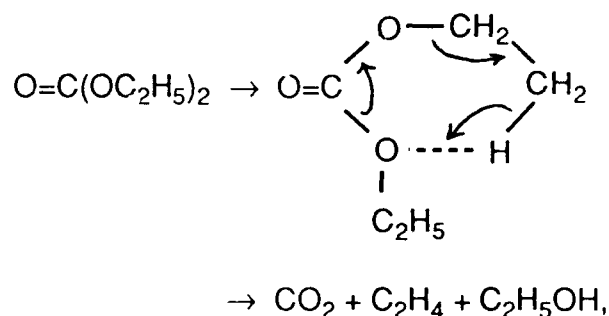
whose unimolecular decomposition constant has been measured to be $k = 7 \times 10^{13} \exp(-46,000/RT)$ s^{-1}. A similar mechanism may indeed be responsible for the production of SiO_2 from $O=Si(OC_2H_5)_2$, accompanying by the generation of additional C_2H_4 and C_2H_5OH.

Since C_2H_5OH is unstable under the conditions employed (T > 720 K, P = 760 torr), it may decompose thermally to produce:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$
$$\rightarrow CH_3 + CH_2OH \rightarrow CH_3 + CH_2O + H$$
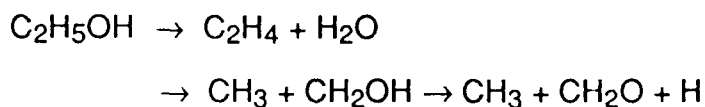
The radical species thus formed may attack TEOS and all molecular products accumulated in the system to produce CO, CH_4 and CH_3CHO, similar to those reactions presented above. Among these secondary products formed, H_2O may have the most profound effect on the acceleration of TEOS decomposition via hydrolysis [9].

$$Si(OC_2H_5)_4 + H_2O \rightarrow HOSi(OC_2H_5)_3 + C_2H_5OH$$
$$HOSi(OC_2H_5)_3 \rightarrow O=Si(OC_2H_5)_2 + C_2H_5OH$$

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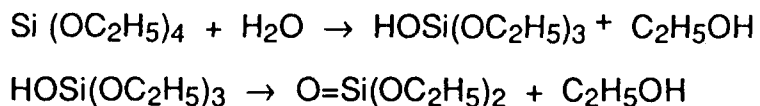
This catalytic process produces additional C_2H_5OH, which in turn generates more H_2O. These secondary reactions, which are not present in the TMOS system, may account for the lowering of the A-factor from a typical value of 5 x 10^{13} - 1 x 10^{14} s^{-1} for a 6 - centered molecular elimination process [10] to 7 x 10^{10} s^{-1} measured in the present experiment. With a low pressure flow method, Ivanov et al. obtained a value as low as 10^6 s^{-1} [6]. We hope to quantify the extent of the H_2O catalysis effect by kinetic modeling.

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Fig 1. Typical TMOS FTIR spectra from 207 torr samples. (A) 0.60% TMOS/Ar mixture pyrolyzed at P=705 torr and T = 940 K for 6 minutes. (B) unpyrolyzed 0.6% TMOS/Ar mixture (C) the difference between (A) and (B).

Fig 2. Typical TEOS FTIR spectra from 239 torr samples. (A) 0.1% TEOS/Ar mixture pyrolyzed at P=725 torr, T=813 K for 6 minutes. (B) unpyrolyzed 0.1% TEOS mixture (C) the difference between (A) and (B).

Fig 3. Concentration-time profiles of various species produced during TMOS thermal decomposition. P = 704 torr, T= 968 K, 0.6% TMOS/Ar mixture.

Fig 4. Concentration - time profiles of various species produced during TEOS thermal decomposition. P = 755 torr, T=820 K, 0.06% TEOS/Ar mixture.

Fig 5. Apparent first order decay plots for TMOS at 858 K, 704 torr (triangle) and TEOS at 820 K, 725 torr (square). The Y axis is mole fraction.

Fig 6. Comparison of TMOS (square) and (triangle) global rate constants.

YIELDS (Mole Fraction)

0.0004

0.0003

0.0002

0.0001

0.0000

TIME (Sec)

0   72   144   216   288   360

□ TEOS
● C2H4
■ CH3CHO
△ CO

10⁻²

Concentration

TMOS

10⁻³

10⁻⁴

TEOS

10⁻⁵

10⁻⁶

0   100   200   300   400

Time/Seconds

y-axis: k / s
x-axis: 1000 / T (K)

TEOS

TMOS