Single-Pulse Shock Tube Study of the Decomposition of Tetraethoxysilane and Related Compounds

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Tetraethoxysilane (TEOS) has been decomposed in single-pulse shock tube experiments over the temperature range 1160−1285 K and pressures of about 150 kPa (1.5 bar). The main observed products are ethylene and ethanol. The yields of these products as a percentage of decomposed TEOS increase with temperature. Studies have also been carried out with tetra-n-propoxysilane (TPOS), dimethyldiethoxysilane (DMDEOS), and trimethylethoxysilane (TMEOS). Evidence is presented that in all cases the main initial reaction is a 1,2-elimination to form the olefin and the corresponding silanol. A smaller contribution from C−C bond-breaking channels is also observed. In combination with lower temperature results and the thermochemistry, the following rate expressions for the elementary processes are recommended: $k[\text{TEOS} \rightarrow C_2H_4 + HOSi(OC_2H_5)_3]$ = $1.04 \times 10^{10}T^{1.1} \exp(-30\,950\ \text{K}/T)\ \text{s}^{-1}$; $k[\text{TEOS} \rightarrow CH_3 + CH_2OSi(OC_2H_5)_3]$ = $4 \times 10^{17} \exp(-43\,300\ \text{K}/T)\ \text{s}^{-1}$. The observed ethanol product is postulated to arise from decomposition of the silanol in a gas phase reaction. A kinetic model which quantitatively accounts for the observed products in the decomposition of TEOS, DMDEOS, and TMEOS has been developed. The model includes radical reactions as well as molecular reactions of the silanol and subsequently formed products, including silicates and silyl acids. The model requires an activation energy of ≤ 200 kJ mol^{-1} for the reaction which forms ethanol from the silanol. Such a low barrier is apparently at odds with recently calculated values for the thermochemistry of some silicon compounds.

Introduction

Tetraethoxysilane (TEOS) is widely used in the semiconductor industry as the precursor for the preparation through chemical vapor deposition (CVD) of thin films of silicon dioxide. As device dimensions shrink into the submicron region, material requirements and deposition conditions become more stringent and there is increasing interest in the understanding of such CVD processes at a more detailed level.[1−4] For high-temperature CVD of silicon dioxide with TEOS, the possibility of gas phase contributions to the overall process cannot be ignored. This is the focus of the present study.

The decomposition of TEOS has been previously studied by Chu et al.[5] in static systems in the 700−820 K range using Fourier transform infrared spectroscopy for the detection of reactant and products. They obtained the following rate expression for decomposition, $k(\text{TEOS}) = 7.4 \times 10^{10} \exp(-24\,900\ \text{K}/T)\ \text{s}^{-1}$, and suggested a six-center transition state leading to the direct formation of ethylene and ethanol. Ethylene was the main observed reaction product. Smaller quantities of acetaldehyde and carbon monoxide were found, and these were presumed to be the decomposition products from ethanol. Studies on tetramethylsilane[6] were also carried out and it was shown that this compound was much less labile than TEOS with rate constants for decomposition a factor of 100 smaller. Subsequently, the same group carried out TEOS decomposition studies[7] in the presence of toluene and obtained $k(\text{TEOS}) = 4.9 \times 10^{13} \exp(-31\,500\ \text{K}/T)\ \text{s}^{-1}$, parameters which at 750 K are 1 order of magnitude smaller than those of the earlier work. Since toluene is a well-established chain inhibitor, these results indicate possible contributions from a radical-induced mechanism in the case without inhibitor.

Takeuchi et al.[2] have studied the decomposition of TEOS in a low-pressure CVD reactor at 950 K and 13 Pa (1 Torr) pressure and inferred the presence of hexaethoxysiloxane from direct mass spectrometric analysis of the products. The collected condensed product showed the presence of ethoxy-based silica in the solid component, while the liquid phase was purely ethanol. The deposition rate profiles were suggestive of two reactive intermediates. A model was recommended for fitting film growth rates. It involves decomposition of TEOS to form ethylene and silanol, and the reaction of the silanol with TEOS to form hexaethoxysiloxane and presumably ethanol in a condensation-like process.

In the present work, experiments are carried out in a heated single-pulse shock tube. This well-established method is especially suited for studying the quantitative details of the initial unimolecular decomposition processes of large polyatomic compounds.[8] The shock heating, short reaction time, and cold walls limit surface contributions to decomposition mechanisms. Analysis of reactants and final stable products by gas chromatography makes possible studies at a very low reactant concentration. This in turn permits the use of chemical inhibitors in large excess and leads to the suppression of radical-induced decomposition. Dilute conditions and the use of inhibitors also allow the use of an internal standard; a unimolecular reaction whose rate expression for decomposition is well known, so as to establish the average reaction temperature. Since disappearance of reactants or the appearance of products are the only consequences of unimolecular decompositions, highly accurate rate expressions for such processes can now be obtained. No claim is made that in actual systems these are the only processes of importance. They do, however, represent a part of the overall reaction which must be understood for simulations based on fundamental chemistry.

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CH$_3$—CH$_2$—O—Si(OCH$_2$CH$_3$)$_3$ CH$_3$—CH$_2$—CH$_2$—O—Si(OCH$_2$CH$_2$CH$_3$)$_3$
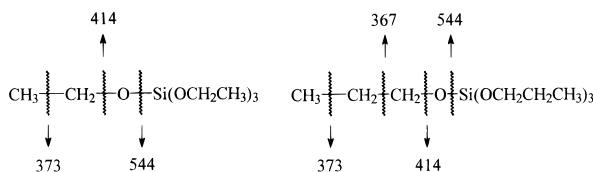
373   544   373   414

Figure 1. Bond energies in TEOS and TPOS in kJ/mol. Data from refs 9 and 10.

TABLE 1: Thermochemistry at 298 K of Some Reactions Involving Direct Formation of Molecules[a]

reaction	enthalpy (kJ/mol)
Si(OC$_2$H$_5$)$_4$ → Si(OC$_2$H$_5$)$_3$OH + C$_2$H$_4$	43.9
Si(OC$_2$H$_5$)$_4$ → O=Si(OC$_2$H$_5$)$_2$ + C$_2$H$_4$ + C$_2$H$_5$OH	335.6
Si(OC$_2$H$_5$)$_3$OH → Si(OC$_2$H$_5$)$_2$(OH)$_2$ + C$_2$H$_4$	49.4
Si(OC$_2$H$_5$)$_3$OH → O=Si(OC$_2$H$_5$)OH + C$_2$H$_4$ + C$_2$H$_5$OH	342.5
Si(OC$_2$H$_5$)$_3$OH → O=Si(OC$_2$H$_5$)$_2$ + C$_2$H$_5$OH	291.6
Si(OC$_2$H$_5$)$_2$(OH)$_2$ → Si(OC$_2$H$_5$)(OH)$_3$ + C$_2$H$_4$	48.5
Si(OC$_2$H$_5$)$_2$(OH)$_2$ → O=Si(OH)$_2$ + C$_2$H$_4$ + C$_2$H$_5$OH	346.0
Si(OC$_2$H$_5$)$_2$(OH)$_2$ → O=Si(OC$_2$H$_5$)OH + C$_2$H$_5$OH	294.2
Si(OC$_2$H$_5$)$_2$(OH)$_2$ → O=Si(OC$_2$H$_5$)$_2$ + H$_2$O	290.8
Si(OC$_2$H$_5$)(OH)$_3$ → Si(OH)$_4$ + C$_2$H$_4$	50.2
Si(OC$_2$H$_5$)(OH)$_3$ → O=Si(OH)$_2$ + C$_2$H$_5$OH	297.5
Si(OC$_2$H$_5$)(OH)$_3$ → O=Si(OC$_2$H$_5$)OH + H$_2$O	294.1
Si(OC$_2$H$_5$)$_2$ → O=Si(OC$_2$H$_5$)OH + C$_2$H$_4$	52.3
O=Si(OC$_2$H$_5$)OH → O=Si(OH)$_2$ + C$_2$H$_4$	52.3

[a] Data are from refs 9 and 10.

In addition to the experiments with TEOS, studies have also been carried out with tetra-*n*-propoxysilane (TPOS), dimethyldiethoxysilane (DMDEOS), trimethylethoxysilane (TMEOS), and tetramethoxysilane (TMOS). The data on these decompositions were necessary in order to elucidate various aspects of the decomposition mechanism. The large number of ethoxy groups in TEOS made separation of the various channels for decomposition difficult, and without the results from the ancillary experiments, assignment of the reaction mechanism would have been much more uncertain.

Figure 1 contains some pertinent bond energies[9,10] in TPOS and TEOS. These can be used to estimate minimum rate constants for bond fission reactions. The weakest bond in TEOS is the C—C bond. For TPOS the C—ethyl bond is the most labile. Decomposition can also proceed by molecular processes, which involve the simultaneous cleavage and formation of a number of bonds. Except by analogies there are no firm bases for predictions of such rates. Ho and Melius[9] have calculated the enthalpies of formation of many of the possible products arising from TEOS decomposition. These results set lower limits on the possible activation energies for the relevant processes. Some pertinent data can be found in Table 1.[9] Particularly important is the very large barrier for the transformation of the silanol into ethanol and silanone and diol into water and silanone (see reactions leading to the formation of Si=O group in Table 1). Thus the calculated thermochemistry predicts extreme difficulties for conversion to ethanol and water under the present conditions. In the analogous organic case such reactions would be virtually instantaneous.

To better understand the effect of silicon on the reactivity of ethoxy compounds, we have recently studied[11] the decomposition of tetraethyl orthocarbonate (TEOC), the carbon analog of TEOS, diethyl carbonate (DEC); and diethoxymethane (DEM). In the case of TEOC, the mechanism involves formation of DEC and equal amounts of ethylene and ethanol. DEC decomposes into equal amounts of ethylene and ethanol, presumably through elimination of ethylene followed by the rapid decomposition of the unstable hydroxyethoxy intermediate. The rate expres-

TABLE 2: Mixtures Used in Present Study[a]

silicon compound	internal standard	inhibitor	additional constituent
420 ppm TEOS	140 ppm 4MCH	1% 135TMB	
420 ppm TEOS	140 ppm 4MCH	1% 135TMB	0.5% TMOS
210 ppm TEOS	70 ppm 4MCH	0.5% 135TMB	
420 ppm TEOS	140 ppm *t*-butanol	1% 135TMB	
200 ppm TMOS	140 ppm tetralin	1% 135TMB	
140 ppm TPOS	140 ppm 4MCH	1% 135TMB	
420 ppm TMEOS	140 ppm *t*-butanol	1% 135TMB	
380 ppm DMDEOS	140 ppm *t*-butanol	1% 135TMB	
420 ppm ethanol	140 ppm *t*-butanol	1% 135TMB	

[a] Argon is the diluent in all mixtures. TEOS = tetraethoxysilane; 4MCH= 4-methylcyclohexene; 135TMB = mesitylene (1,3,5-methylbenzene); TMOS = tetramethoxysilane; tetralin = 1,2,3,4-tetrahydronaphthalene; TPOS = tetrapropoxysilane; TMEOS = trimethylethoxysilane; DMDEOS = dimethyldiethoxysilane.

sions for the overall unimolecular decomposition processes are

$$k(\text{TEOC}) = 8.1 \times 10^{13} \exp(-27\,485\ \text{K}/T)\ \text{s}^{-1}$$

$$k(\text{DEC}) = 1.1 \times 10^{13} \exp(-23\,290\ \text{K}/T)\ \text{s}^{-1}$$

$$k(\text{DEM}) = 8.6 \times 10^{15} \exp(-36\,120\ \text{K}/T)\ \text{s}^{-1}$$

where the decomposition channels for DEM are

$$k(\text{DEM} \rightarrow \text{ethylene} + \text{HOCH}_2\text{OC}_2\text{H}_5) = 1.2 \times 10^{15} \exp(-34\,520\ \text{K}/T)\ \text{s}^{-1}$$
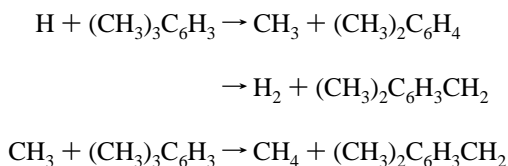
$$k(\text{DEM} \rightarrow \text{C}_2\text{H}_5 + \text{OCH}_2\text{OC}_2\text{H}_5) = 2.1 \times 10^{16} \exp(-38\,214\ \text{K}/T)\ \text{s}^{-1}$$

The results on DEC are in excellent agreement with lower temperature data. An important feature of these results is the factor of 20 difference in rate constants between TEOC and DEM under our reaction conditions and the very large A-factor for DEM decomposition. Furthermore, unlike the situation for DEC and TEOC, in DEM decomposition much more ethylene was formed in comparison to ethanol. This suggests that, aside from molecular decomposition to form ethylene, in this case C—C bond cleavage also makes a contribution. Aside from the rate data, a key consequence of these studies is the validation of the analytical procedure.

Experimental Section[12]

Our experiments were carried out in a heated single-pulse shock tube designed to study relatively nonvolatile compounds. The shock tube and the associated gas handling and sample transfer system were all maintained at 108 °C. Analysis of the reactants and products was by gas chromatography using a wide bore, 30 m carbowax capillary column in the programmed temperature mode for the determination of the heavier components and a 2 m × 1 mm i.d. column packed with Hayesep S combined with a 1 m × 1 mm i.d. column packed with Hayesep N for the lighter species. Samples are transferred from the shock tube to the gas chromatograph using a series of valves and sample loops.

Table 2 contains a list of the mixtures that have been tested. Variations of the nature of the mixtures and their relative concentrations provide a means of confirming the postulated mechanisms. Mesitylene (1,3,5-trimethylbenzene) is used as the chemical inhibitor. It inhibits chain processes through the reactions

$$H + (CH_3)_3C_6H_3 \rightarrow CH_3 + (CH_3)_2C_6H_4$$

$$\rightarrow H_2 + (CH_3)_2C_6H_3CH_2$$

$$CH_3 + (CH_3)_3C_6H_3 \rightarrow CH_4 + (CH_3)_2C_6H_3CH_2$$

Thus highly reactive hydrogen and methyl radicals are converted to much less reactive benzyl-type radicals. The main mode of disappearance of benzyl-type radicals is through combination with other radicals and thus represents another chain inhibition pathway.

Standard Reactions. For the experiments at lower temperatures, we used the well-known decomposition of 4-methylcyclohexene to propylene and butadiene as the internal temperature standard ($k = 2 \times 10^{15} \exp(-33\,500\ K/T)\ s^{-1}$).[8] At temperatures above 1225 K, t-butanol was used as the temperature standard. For its decomposition to isobutene and water we used the data of Newman et al.,[13] who determined the rate constant relative to that for cyclohexene decomposition. To ensure self-consistency with the experiments with the 4-methylcyclohexene standard, we have used the parameters for cyclohexene decomposition from ref 8, rather than the slightly different values used by Newman et al. This leads to $k(t\text{-butanol} \rightarrow \text{isobutene} + H_2O) = 6.0 \times 10^{14} \exp(-33\,640\ K/T)$. At the temperatures of our study, a second channel, t-butanol $\rightarrow CH_3 + (CH_3)_2COH \rightarrow$ acetone $+ H + CH_3$, becomes important enough that it must be taken into account. From the measured t-butanol, isobutene, and acetone concentrations, the average reaction temperature can be calculated by the relation

$$\ln([t\text{-butanol}]_i/[t\text{-butanol}]_f) =$$
$$\tau(1 + [\text{acetone}]_f/[\text{isobutene}]_f) \times$$
$$(6.0 \times 10^{14} \exp(-33\,640\ K/T))$$

where the subscripts i and f refer to initial and final concentrations, τ is the residence time of about 500 μs, T is the reaction temperature, and the rate expression is that for the isobutene channel.

Chemicals. Mesitylene, t-butanol, and TEOS were purchased from Aldrich chemicals and 4-methylcyclohexene from Wiley Organics, while TMOS, TPOS, TMEOS, and DMDEOS were from United Chemical Technologies. Except for vigorous degassing and removing of ethanol from the ethoxysilanes by a 0.2 nm molecular sieve, they have been used without further purification. The argon from Matheson was of ultrapure grade.

Results

The main detectable stable products from the decomposition of TEOS were ethylene and ethanol. Acetaldehyde, if present at all, is in much smaller concentrations. We were unable to find any chromatographic peaks corresponding to silicon-containing products. Figure 2 gives the results in terms of C2 yields as a function of the amount of TEOS consumed. It can be seen that at the lowest extents of reaction slightly over 1 ethylene is produced for every TEOS reacted. Only about 0.3 ethanol is found for every TEOS destroyed. At higher temperatures more C2 products are formed relative to the amount of TEOS consumed. The rate of increase is at first similar for ethanol and ethylene. However, at about 1250 K, the relative yields of ethylene show a more rapid increase while those of ethanol flatten out. Per reacted TEOS, at the lower temperatures we recover only about 40% of the available ethoxy groups as C2 products, while at the highest temperatures this value increases to 75%. Although we find some CH_4, indicating the release of methyl radicals into the system, the total amount of methane does not compensate for the deficit in C2 formation.
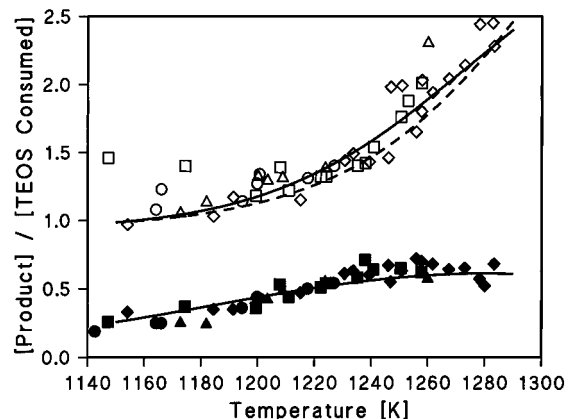

Figure 2. Yields of ethylene (open symbols) and ethanol (filled symbols) as a fraction of decomposed TEOS as a function of temperature. Symbols: ($\bigcirc$, $\bullet$) 420 ppm TEOS, 140 ppm 4-methylcyclohexene, 1% mesitylene in argon; ($\square$, $\blacksquare$) 420 ppm TEOS, 0.5% TMOS, 140 ppm 4-methylcyclohexene, 1% mesitylene in argon; ($\triangle$, $\blacktriangle$) 210 ppm TEOS, 70 ppm 4-methylcyclohexene, 0.5% mesitylene in argon; ($\diamond$, $\blacklozenge$) 420 ppm TEOS, 140 ppm t-butanol, 1% mesitylene in argon. Solid lines are fits using the data in Table 3. Dotted lines are fits based on the data in Table 4, assumming that ethanol is not formed in a gas phase process during the shock. Reaction pressures are 1.5−2 bar.
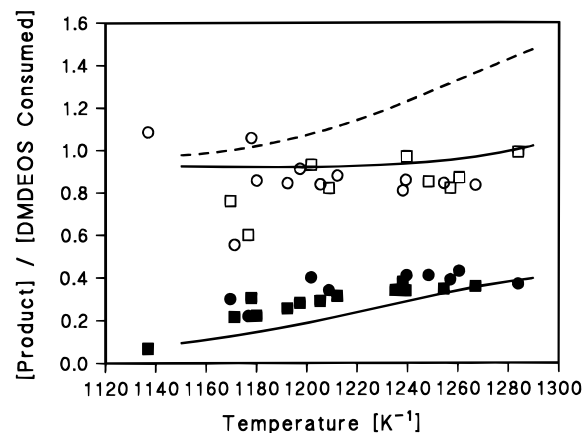

Figure 3. Yields of ethylene (open symbols) and ethanol (filled symbols) as a fraction of decomposed DMDEOS as a function of temperature. Symbols: ($\bigcirc$, $\bullet$) 380 ppm DMDEOS, 140 ppm t-butanol, 1% mesitylene in argon; ($\square$, $\blacksquare$) 480 ppm DMDEOS, 150 ppm t-butanol, 1% mesitylene. Solid lines are based on the mechanism in Table 3. Dotted lines are based on data in Table 4 where we have assumed that ethanol is not formed in a high-temperature gas phase process. Reaction pressures are 1.5−2 bar.

The presumption is that substantial amounts of carbon are still bonded to the silicon after the initial decomposition step.

Figure 3 contains the corresponding results for dimethyldiethoxysilane (DMDEOS). Considerable similarities to the TEOS system are observed. It is interesting that the two sets of data for DMDEOS were taken over a year apart, using different shock tubes, transfer lines, and gas chromatographic columns. Note that one set of data was taken with a shock tube constructed out of aluminum with transfer lines to the gas chromatograph of nickel 200, while the other set utilized a stainless steel shock tube with transfer lines of fused silica. The reproducibility of the data is evidence that the results are not strongly influenced by the nature of these surfaces. This is important since the possibility of surface-mediated decomposition of silicon-containing intermediates prior to analysis is of some concern, particularly with regard to ethanol formation.

The results on trimethylethoxysilane (TMEOS), summarized in Figure 4, show that ethylene is the only C2 product and its recovery in terms of available ethoxy groups is about 85%. In
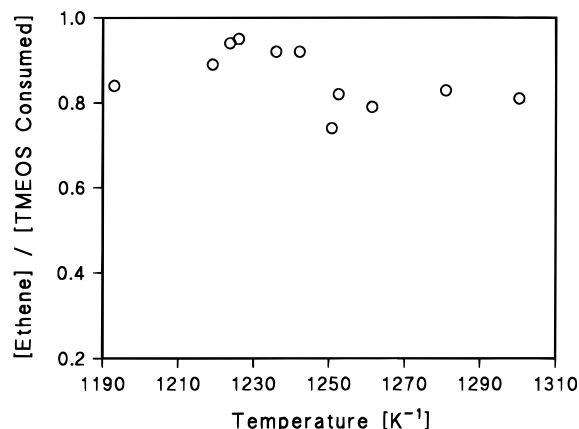
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Figure 4. Yields of ethylene as a fraction of decomposed TMEOS as a function of temperature. The mixture contains 420 ppm TMEOS, 140 ppm *t*-butanol, and 1% mesitylene in argon. No ethanol was found. Reaction pressures are 1.5−2 bar.
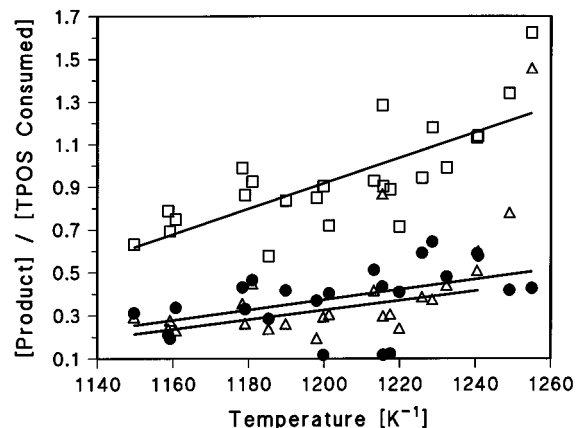

Figure 5. Yields of ethylene (□), propylene (△), and propanol (●) as a fraction of decomposed TPOS as a function of temperature. The mixture contains 140 ppm TPOS, 140 ppm 4-methylcyclohexane, and 1% mesitylene in argon. Reaction pressures are 1.5−2 bar.

this case the yield of ethylene per reacted TMEOS does not increase with temperature and indeed may even decrease slightly over the temperature range.

Figure 5 contains data on the distribution of products from the decomposition of tetra-*n*-propoxysilane (TPOS) expressed in terms of products formed per TPOS destroyed. The low volatility of this compound is just about at the limit where quantitative results can be obtained in our apparatus. We believe this to be the primary reason for the large scatter in the data. The detection of propylene and 1-propanol in ratios similar to those of ethylene and ethanol from the ethoxy compounds is indicative of a similar decomposition mechanism. Also detected were smaller amounts of ethylene. As we will see, we believe this product results from a C−C bond fission channel that is occurring parallel to a molecular process.

Some experiments were carried out with tetramethoxysilane (TMOS). We found the rate constant for its decomposition to be much smaller than that of TEOS, confirming the results[6] of Chu et al. In additional studies, TEOS was decomposed in the presence of a large excess of TMOS. These experiments were designed to test the suggestion[2] of Takeuchi et al. that condensation reactions of silanols with alkoxy silanes are important. If this were the case in our system, reactions of e.g. triethoxysilanol would release methanol through the process $(C_2H_5O)_3SiOH + TMOS \rightarrow (C_2H_5O)_3SiOSi(OCH_3)_3 + CH_3OH$. No methanol or change in ethanol production could be found. This rules out the possibility that the observed alcohols are formed via a condensation reaction of some product with
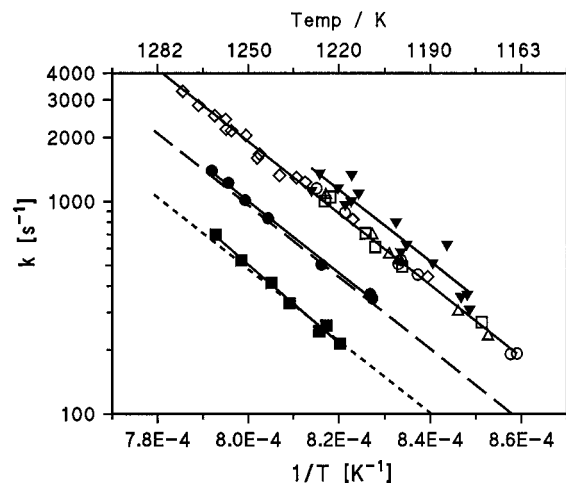

Figure 6. Arrhenius plots for the decompositions of TEOS, DMDEOS, TMEOS and TPOS. Symbols for TEOS: (○) 420 ppm TEOS, 140 ppm 4-methylcyclohexene, 1% mesitylene in argon; (□) 420 ppm TEOS, 0.5% TMOS, 140 ppm 4-methylcyclohexene, 1% mesitylene in argon; (△) 210 ppm TEOS, 70 ppm 4-methylcyclohexene, 0.5% mesitylene in argon; (◇) 420 ppm TEOS, 140 ppm *t*-butanol, 1% mesitylene in argon. Symbol for DMDEOS: (●); 380 ppm DMDEOS, 140 ppm *t*-butanol, 1% mesitylene in argon. Symbol for TMEOS: (■), 420 ppm TMEOS, 140 ppm *t*-butanol, 1% mesitylene in argon. Symbol for TPOS: (▼), 140 ppm TPOS, 140 ppm MCH, 1% mesitylene in argon. The dashed lines are drawn at one-half and one-fourth the rate expression for TEOS.

the starting alkoxysilane. Note that this conclusion applies both to gas phase processes and to any possible surface-mediated reaction. This does not necessarily invalidate the mechanism[2] outlined by Takeuchi et al. since the conditions are different. It does suggest, however, that if the condensation process occurs it must be at the hot walls of the low-pressure CVD reactor.

Figure 6 summarizes the data on the rate constants for the decomposition of the compounds that have been studied. Since we were unable to find any silicon-containing products, these rate constants are necessarily based on reactant disappearance instead of product appearance. This can lead to rate expressions of lower precision since at low conversions two large numbers are being subtracted. The following rate expression for TEOS has been obtained

$$k(\text{TEOS} \rightarrow \text{products}) = 6.7 \times 10^{16} \exp(-38\,970 \text{ K}/T) \text{ s}^{-1}$$

where the uncertainties in the results are factors of 4 in the A-factor, 1700 K in the activation energy, and 25% in the rate constants. Also included in Figure 6 are lines that are one-half and one-quarter of the rate constant for TEOS. It can be seen that they intersect the experimental results of DMEOS and TMEOS, suggesting that the decomposition rate scales directly with the number of ethoxy groups in the molecule. From the TPOS data, we see that substituting the ethoxy groups by *n*-propoxy slightly increases the decomposition rate. Not enough rate data have been accumulated for the compounds other than TEOS so as to obtain reliable rate expressions.

In the course of the work it became necessary to obtain information on the thermal stability of the ethanol that is formed. Data on this issue are summarized in Figure 7. We find the rate expression $k(C_2H_5OH \rightarrow \text{products}) = 8.5 \times 10^{13} \exp(-33\,372 \text{ K}/T) \text{ s}^{-1}$. It is likely that this decomposition process is in the pressure-dependent region. From our data the branching ratio for elimination of water versus C−C bond cleavage is estimated to be 0.75. For present purposes we are only interested in its stability under the present reaction conditions.
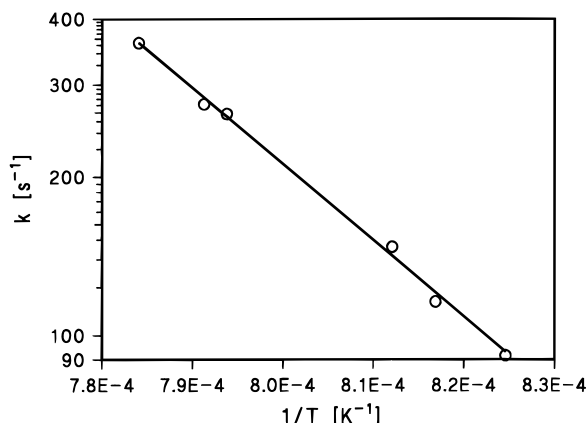
Figure 7. Rate constants for ethanol decomposition. Reaction pressures are 1.5−2 bar. Rate expression fitting data is $8.5 \times 10^{13} \exp(-33\ 372\ K/T)\ s^{-1}$.

Discussion

The failure to account for all the organic ligands especially at the lower temperatures is evidence that the initial products containing silicon are stable in the gas phase. It is noteworthy, therefore, that we were unable to detect any such products in our gas chromatography (GC) analyses. Such products apparently react in some manner either prior to or during the GC analysis. In this regard it is important to realize that any decomposition process that occurs during the GC analysis itself will not affect our analytical results for ethylene and ethanol. Because the GC column very rapidly separates the light C2 compounds from the heavier silicon-containing organics, any C2's formed by decomposition of the silicon species on the column will emerge at different times from those C2 species present at the time of injection. Thus, for any hypothetical surface reaction to affect our analyses for the alcohols and alkenes, it must occur either in the shock tube or gas-handling system prior to injection. The absence of methanol product in the experiments with TEOS in the presence of excess TMOS clearly demonstrates that condensation reactions of silanols are not occurring in either the gas phase or on the surface prior to the analysis. The reproducibility of the data for DMDEOS (Figure 3) further demonstrates that changing the surface of the shock tube or transfer line did not affect the results. Finally, we note that unsaturated silicon compounds form weak π-bonds and are extremely reactive. However, simple polymerization of such species occurs without further loss of ligands: $n(R_2\text{-}Si{=}O) \rightarrow [-(R)_2Si-O-]_n$. Thus, even if occurring, such processes are not expected to affect the results for the C2 species. While it is impossible to completely rule out some surface effect, we have been unable to find evidence for such a process and for the moment assume that our results on ethylene and ethanol formation pertain to gas phase reactions.

The data summarized in the Results section are numerous and, taken together, provide considerable insight into the details of TEOS decomposition. Nonetheless, it is clear that the reaction is complex. In Figure 8 a general mechanism for TEOS decomposition is put forth and it will be useful to refer to this during the Discussion. The following will contain a justification of the various steps in the mechanism in terms reproducing our results. Because of the general complexity, we will break the Discussion into several sections. We will begin with some of the qualitative features. Thereafter we will consider the quantitative aspects and develop a kinetic model. Finally, we will return to the question of surface effects and draw some final conclusions.

Mechanisms. *Initial Processes.* Possible initial processes in the decomposition of TEOS and related ethoxy compounds include molecular elimination reactions and bond fissions. As indicated by Figure 1, the Si−O and C−O bonds are quite strong. This is confirmed experimentally by the observed high stability of TMOS. It is apparent that the preferred bond cleavage in ethoxy silane compounds is of the C−C bond. Fission of this bond cannot easily lead to the observed ethylene as a major initial product, which suggests there must be a direct
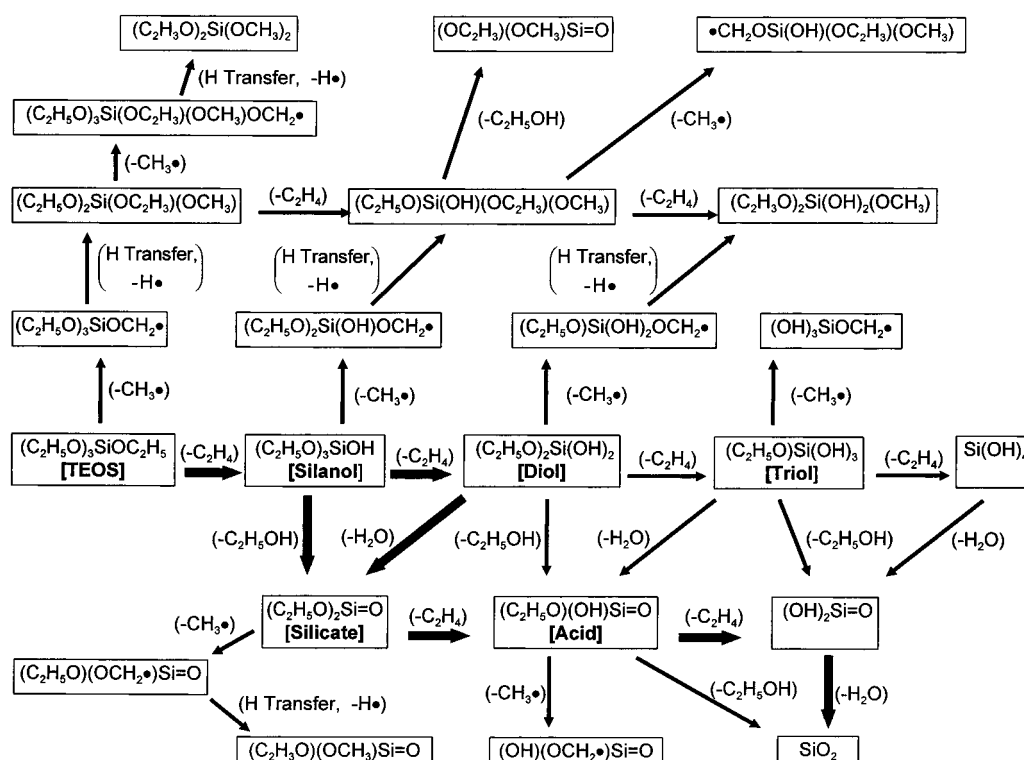

Figure 8. Suggested pathways for the formation of ethanol and ethylene during the inhibited thermal decompositon of TEOS in single-pulse shock tube experiments. Bold arrows indicate the most important reaction pathways based on the model given in Table 3.

molecular channel for alkene generation. An even stronger argument can be made from the large ratios of propylene to ethylene in TPOS decomposition, since propylene is the expected product of a molecular reaction while the main ethylene source is probably from C−C bond breaking.

The data in Figure 6 demonstrate that the rate constants for decomposition are proportional to the number of ethoxy groups present in the starting material. This suggests that the mechanisms are similar for the silicon compounds. It is also in interesting contrast to the ethoxy carbon compounds, where the tetraethoxy compound decomposed with rate constants[11] a factor of 20 larger than diethoxymethane and with important differences in the distribution of the stable compounds. Further indication of the similarities in mechanism for the silicon compounds is the correspondence of the relative yields of ethylene and ethanol in the decomposition of TEOS and DMDEOS in the lower temperature regime. From Figure 5 it can be seen that similar alkene to alcohol product ratios are also observed in the experiments with TPOS.

Chu et al. have suggested[5] a six-center decomposition of TEOS leading to the formation of equal amounts of ethanol and ethylene:
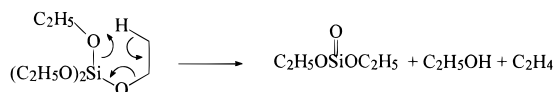

This mechanism would suggest an alkene to alcohol ratio of 1, at least in the early stages of reaction. This is in conflict with the data. It is also incompatible with the direct scaling of the decomposition rate constants with the number of ethoxy groups. TEOS, for example, has 36 equivalent six-center transition states, compared with six for DMDEOS and none for TMEOS, yet the respective relative rates are 4:2:1. The most likely alternative is a four-center 1,2-elimination reaction leading to alkene and silanol:

$$TEOS \rightarrow C_2H_4 + (C_2H_5O)_3SiOH$$
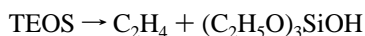
In contrast to the six-center process, this mechanism is compatible with the observed rates and product ratios, provided the formation of ethanol can be explained.
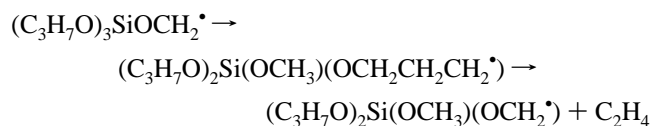
An important mechanistic clue is the failure to detect ethanol in TMEOS decomposition. This indicates that two ethoxy groups are necessary for its formation. While it is possible that the six-center elimination reaction could be a slower process occurring in parallel with the four-center reaction, if this were the case one would expect that the ethylene to ethanol ratios would be significantly different for TEOS and DMDEOS. The fact that at the lower temperatures the C2 ratios for these two substrates are nearly the same suggests that the six-center transition state is not an important initial reaction. Since it is difficult to envision other direct routes to ethanol formation, this observation also indicates that ethanol must be formed in a secondary process.

Although the molecular elimination appears to be the primary initial reaction, contributions from a bond-breaking channel are suggested by the failure to account for all the disappeared TMEOS in terms of ethylene yields. Even more definitive is the presence of C_2H_4 from the decomposition of TPOS. There is no known molecular mechanism that can account for its formation, and the ethylene must arise through C−C bond fission:

$$TPOS \rightarrow (C_3H_7O)_3SiOCH_2 + C_2H_5$$

$$C_2H_5 \rightarrow C_2H_4 + H$$
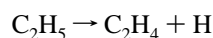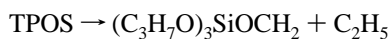
The observation that the propylene to ethylene ratios are much greater than 1 indicates that the bond-breaking channel must make a relatively small contribution to the overall decomposition. This is further confirmed by the fact that TPOS decomposes only slightly faster than TEOS. If bond breaking were a more important mode, one would expect a much larger effect on the basis of the bond energies given in Figure 1.

To obtain a reliable estimate of the branching ratio for the molecular and bond fission channels from the TPOS decomposition data, we would have to know how many ethylenes arise from each initial bond fission reaction. Unfortunately, the initial silicon-containing radical may isomerize and be a source of additional C_2H_4:

$$(C_3H_7O)_3SiOCH_2^\bullet \rightarrow$$
$$(C_3H_7O)_2Si(OCH_3)(OCH_2CH_2CH_2^\bullet) \rightarrow$$
$$(C_3H_7O)_2Si(OCH_3)(OCH_2^\bullet) + C_2H_4$$

This is not the only pathway for this radical, however, so any estimate based on this data would have a large uncertainty. For a better estimate of the branching ratio we must rely on the data from the TMEOS decomposition. In this case the thermochemistry dictates that all the ethylene arises from the initial molecular elimination. The difference between the total rate and that for ethylene formation can only arise from the C−C bond-breaking process. The TMEOS data suggest a 10−15% contribution from the C−C bond fission channel.

To summarize, our data indicate two primary initial channels for TEOS decomposition. A four-center molecular decomposition to form ethylene and triethoxysilanol is the major process. Parallel to this is cleavage of the C−C bond, leading to the generation of a methyl radical and the $(C_3H_7O)_3SiOCH_2$ radical. Even at the high temperatures of our study, C−C bond fission is a minor channel. Nonetheless, it does release radicals and in a noninhibited system could result in the rapid decomposition of TEOS through chain processes.

Decomposition of Intermediates. Obviously there is no reason that the molecules cannot react further following expulsion of the first ethylene. Until all C2 groups are removed, at least some of the subsequent channels may lead to additional ethylene formation. That such processes occur is suggested by the increase in the relative yield of ethylene with the number of ethoxy groups in the starting compound. This is particularly apparent at higher degrees of conversion, where secondary processes would be most important.

We have postulated alkoxy silanols to be primary initial products, with alcohol formation occurring in a secondary step. If the reactivity of the silanols was similar to their carbon analogs,[11] one would expect them to decompose immediately to a silicate and alcohol, e.g.

$$(C_2H_5O)_3SiOH \rightarrow C_2H_5OH + (C_2H_5O)_2Si{=}O$$
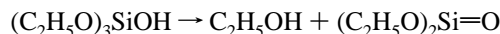
However, as can be seen from Table 1, the calculations of Ho and Melius[9] indicate very high thermodynamic barriers for such reactions. Thus, the detection of ethanol in TEOS and DMDEOS decompositions and propanol from TPOS is a very important and somewhat surprising result. The experiments with TEOS in the presence of large quantities of TMOS were designed to test for possible second-order processes such as $(C_2H_5O)_3SiOH + TMOS \rightarrow (C_2H_5O)_3SiOSi(OCH_3)_3 + CH_3OH$. The lack of methanol formation or change in the TEOS products is a clear indication that such processes are not occurring either on a surface or in the gas phase. As in all mechanistic questions, we cannot rule out the possibility that one of the undetected gas phase reaction products may react

subsequent to the heating period on the cold walls of the shock tube or sampling system to produce the ethanol. However, the thermodynamic constraints of Ho and Melius mean that in no case can ethanol be produced in a process (surface or gas) that involves the formation of the silicate since this is the source of the high endothermicity. A possible alternative would involve the reaction of the silanols with water leading to the formation of the alcohol and diol. This implies water as an impurity in the system. In this regard, TEOS itself is readily hydrolyzed in solution to produce silanol and ethanol, yet in control experiments with unshocked mixtures no such reaction was observed. This would require either that significant water is not intrinsically present in our system, or that such reactions do not readily occur on the surfaces. Of course water may also be produced in the latter stages of TEOS decomposition and could conceivably have an effect. However, in the studies with *t*-butanol as the standard, an additional source of water was present but no effect on ethanol yields was observed. This sets a lower limit to how much water is needed to cause any effects.

Our failure to find any indication of bimolecular processes or surface effects leads to the conclusion that ethanol is directly formed in a gas phase unimolecular process. This belief rests essentially on the reproducibility of the results despite variations in conditions and, indeed, in the molecules studied. Past experience has shown that for similar situations where subsequent surface effects may be important, as in the decomposition of ethyl phosphates,[14] the yields of ethanol showed enormous variations and were in effect irreproducible. It surface reactions are unimportant, the process responsible for ethanol production must be molecular in nature, since we are unaware of any radical process that could lead to its formation under our conditions.

An interesting aspect of the data in Figure 2 is that the ethylene yields increase rapidly at temperatures above 1250 K, while those for ethanol level off. Our experiments with ethanol demonstrate that it is stable under our conditions, so this behavior is directly related to the decomposition mechanism. It is further significant that the yields of ethanol from DMDEOS and TEOS are very similar. This suggests that only one ethoxy group in TEOS is available for conversion to ethanol. When this is coupled with the increase in ethylene yields in TEOS decomposition at temperatures in excess of 1250 K and the absence of such effects in DMDEOS decomposition, the implication is that one ethanol is expelled from TEOS in a relatively early process, but thereafter the reactions favor ethylene formation. One possible explanation is that the ethanol arises from decomposition of the silanol, but that products of this reaction do not easily produce further ethanol.

The formation of ethanol from silanol is accompanied by the formation of a silicate. The analogous carbon compound is diethyl carbonate (DEC). DEC has a very facile decomposition channel,[11] the retro-ene process, leading to the formation of ethylene and $C_2H_5OCO_2H$, which decomposes immediately to ethanol and CO_2. The silicate may also undergo such a process:
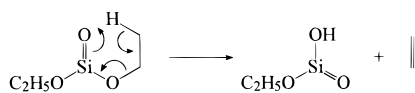
Note that the products are the same as for the four-center elimination of ethylene, but that the reaction may be very much faster. Except, by analogy with the carbon compounds, there is unfortunately no basis for assigning rate constants for such a process. A similar reaction path is also available for decomposition of $C_2H_5OSiO_2H$.

Fission of the C−C bond was shown to be one of the initial processes. In TEOS, this leads to the $(CH_3CH_2O)_3SiOCH_2$

radical and Figure 8 contains a possible mechanism for its decomposition. In the case of the hydrocarbon analog, C−O β-bond fission would clearly be the prevalent channel. However, in view of the strength of the Si−O bond, a more likely pathway for the silicon compound is isomerization to form $(CH_3CH_2O)_2Si(OCH_3)OCH_2CH_2$ and $(CH_3CH_2O)_2(OCH_3)SiOCHCH_3$ radicals via 1−6 or 1−5 hydrogen transfers. For hydrocarbon systems the 1−5 H transfer would be the preferred channel and would lead to C−O β-bond fission and acetaldehyde formation. However, in the silicon compounds the strength of the C−O and Si−O bonds leads to the conclusion that decomposition through the ejection of a hydrogen atom would be favored.

Rate Constants. *Molecular Elimination.* The data given above on TMEOS suggest that near 1250 K the ethylene elimination reaction makes at least an 85% contribution to the overall decomposition of TEOS. This is equivalent to a rate constant for C_2H_4 elimination from TEOS of 1600 s^{-1}. In our work[11] on diethoxymethane decomposition, the rate expression for ethylene elimination leads to a rate constant of 1200 s^{-1} at 1250 K. Since diethoxymethane contains only two ethoxy groups, this suggests that silicon for carbon substitution decreases the rate constant by a factor of 1.5. Assuming that this is largely due to a change in the activation energy, we derive the rate expression

$$k[\text{TEOS} \rightarrow C_2H_4 + (C_2H_5O)_3SiOH] = \\ 2.0 \times 10^{15} \exp(-34\,900\ K/T)\ \text{s}^{-1}$$

This rate expression is somewhat different from that derived by Chu et al. at temperatures near 800 K, $k(\text{TEOS}) = 4.9 \times 10^{13} \exp(-31\,500\ K/T)$ s^{-1}. Extrapolating their results to our temperature range leads to a rate constant that is a factor of 2 smaller than ours. On the other hand, extrapolation of our expression to their temperatures leads to a rate constant that is a factor of 2 smaller than their value. Part of this deviation may arise from the curvature in the Arrhenius plot over 7 orders of magnitude in the rate constant. Indeed, a $T^{1.1}$ curvature in the Arrhenius plot will accommodate all the results. This then leads to a rate expression of

$$k[\text{TEOS} \rightarrow C_2H_4 + (C_2H_5O)_3SiOH] = \\ 1.04 \times 10^{10} T^{1.1} \exp(-30\,950\ K/T)$$

Bond Fission. If we assume that the remaining component is purely bond breaking, then the rate constant at 1250 K is 400 s^{-1}. With a typical A-factor for breaking four C−C bonds of 4×10^{17} s^{-1} we find that an activation energy of 360 kJ/mol is required. This is in reasonable accord with what can be expected from Figure 1. However, this rate constant is based on the subtraction of two large numbers, and errors as large as a factor of 2 are possible.

The sum of the elimination and bond-breaking processes unfortunately does not reproduce the temperature dependence that we have determined from the total disappearance of TEOS. The deviations are about 15% at each end of the temperature range. This should have minimal consequences on our assigned rate constant for elimination. It may have more serious consequences regarding the bond-breaking process. It is conceivable that there are other but unknown processes contributing to TEOS decomposition. Two possibilities are that there are contributions from radical chain induced decomposition at the highest temperatures and that our estimated rate expression for bond breaking may be too small.

Results from Simulations. *Models with Gas Phase Formation of Ethanol.* The mechanism in Figure 8 involves numerous reactions. The experiments described here yield direct results

TABLE 3: Rate Constants Used in Reproducing Experimental Results in Figure 2[a]

reaction	$\log A$ (s^{-1})	E/R (K^{-1})
Si(OC₂H₅)₄(TEOS) → C₂H₄ + Si(OC₂H₅)₃OH (silanol)	**15.3**	**34 500**
Si(OC₂H₅)₄(TEOS) → CH₃ + CH₂OSi(OC₂H₅)₃	**17.6**	**43 300**
Si(OC₂H₅)₃OH (silanol) → C₂H₄ + Si(OC₂H₅)₂(OH)₂ (diol)	15.2	34 500
Si(OC₂H₅)₃OH (silanol) → C₂H₅OH + O=Si(OC₂H₅)₂ (silicate)	11.7	22 700
Si(OC₂H₅)₃OH (silanol) → CH₃ + CH₂OSi(OC₂H₅)₂OH	17.5	43 300
Si(OC₂H₅)₂(OH)₂ (diol) → C₂H₄ + Si(OC₂H₅)(OH)₃ (triol)	15.0	34 500
Si(OC₂H₅)₂(OH)₂ (diol) → H₂O + O=Si(OC₂H₅)₂ (silicate)	11.7	20 000
Si(OC₂H₅)₂(OH)₂ (diol) → C₂H₅OH + O=Si(OC₂H₅)OH (acid)	11.8	22 700
Si(OC₂H₅)₂(OH)₂ (diol) → CH₃ + CH₂OSi(OC₂H₅)(OH)₂	17.3	43 300
Si(OC₂H₅)(OH)₃ (triol) → C₂H₄ + Si(OH)₄	14.8	34 500
Si(OC₂H₅)(OH)₃ (triol) → H₂O + O=Si(OC₂H₅)OH (acid)	11.7	20 000
Si(OC₂H₅)(OH)₃ (triol) → C₂H₅OH + O=Si(OH)₂	11.7	22 700
Si(OC₂H₅)(OH)₃ (triol) → CH₃ + CH₂OSi(OH)₃	17.0	43 300
O=Si(OC₂H₅)₂ (silicate) → C₂H₄ + O=Si(OC₂H₅)OH (acid)	13.0[b]	26 200[b]
O=Si(OC₂H₅)₂ (silicate) → C₂H₄ + O=Si(OC₂H₅)OH (acid)	15.0[c]	34 500[c]
O=Si(OC₂H₅)₂ (silicate) → CH₃ + CH₂OSiO(OC₂H₅)	17.3	43 300
O=Si(OC₂H₅)OH (acid) → C₂H₄ + O=Si(OH)₂	12.7[b]	26 200[b]
O=Si(OC₂H₅)OH (acid) → C₂H₄ + O=Si(OH)₂	14.7[c]	34 500[c]
O=Si(OC₂H₅)OH (acid) → C₂H₅OH + SiO₂	11.2	23 700
O=Si(OC₂H₅)OH (acid) → CH₃ + CH₂OSiO(OH)	17.0	43 300
CH₂OSi(OC₂H₅)₃ → CH₃OSi(OC₂H₅)₂(OC₂H₃) + H	fast	
CH₂OSi(OC₂H₅)₂OH → CH₃OSi(OC₂H₅)(OC₂H₃)OH + H	fast	
CH₂OSi(OC₂H₅)(OH)₂ → CH₃OSi(OC₂H₃)(OH)₂ + H	fast	
CH₃OSi(OC₂H₅)₂(OC₂H₃) → C₂H₄ + CH₃OSi(OC₂H₅)(OC₂H₃)OH	15.0	34 500
CH₃OSi(OC₂H₅)₂(OC₂H₃) → CH₃ + CH₂OSi(OC₂H₅)(OC₂H₃)(OCH₃)	17.3	43 300
CH₂OSi(OC₂H₅)(OC₂H₃)(OCH₃) → Si(OCH₃)₂(C₂H₃)₂ + H	fast	
CH₃OSi(OC₂H₅)(OC₂H₃)OH → C₂H₄ + CH₃OSi(OC₂H₃)(OH)₂	14.7	34 500
CH₃OSi(OC₂H₅)(OC₂H₃)OH → CH₃ + CH₂OSi(OCH₃)(OC₂H₃)OH	17.0	43 300
CH₃OSi(OC₂H₅)(OC₂H₃)OH → C₂H₅OH + CH₃OSi(O)OC₂H₃	11.2	22 700
C₂H₅OH → C₂H₄ + H₂O	13.8	33 300
C₂H₅OH → CH₃ + CH₂OH	16.0	41 800

[a] Reactions in bold type are those on which we could obtain direct experimental information (see text). [b] Refers to retro-ene reaction. [c] Refers to four-center elimination reaction.

only on the two initiating processes. In deriving those results the temperature dependencies of the ethylene and ethanol yields were not used. It is thus of some interest to see whether the C2 yields can be reproduced on the basis of reasonable assumptions and whether there are some special features of the data that emphasize the importance or unimportance of particular reactions. Constraints can be set on some of the possible rate constants by assigning as a first guess the same rate expressions for similar type reactions. For example, we assume that all C—C bond-breaking and four-center ethylene elimination reactions have the same rate parameters, and these are taken from our results on the initial channels. No direct information is available for the ethanol formation reaction or for decompositions of the silicate and acid. Aside from thermochemical kinetic constraints on the A-factors, these rate expressions are thus adjusted to best fit the results. A further constraint is that the assumptions used to fit the TEOS data must be consistent with those used in fitting the data from DMDEOS.

Table 3 contains the rate expressions that are used in making the fit. There is of course a lack of uniqueness to such a procedure, and the ambiguous nature of such models must be recognized. Nonetheless such models form a starting point for a more detailed understanding of the overall reaction. Rate expressions of particular importance in our model are those for ethanol formation and decomposition of the silicate and acid. It is the balance of these reactions that is responsible for the increase in ethylene and flattening of the ethanol yields at temperatures in excess of 1250 K. We postulate that the ethanol arises from elimination reactions from silanol. This leads to formation of the silicate, which has no obvious molecular channels other than elimination of ethylene. To reproduce the tapering off of the ethanol yields at higher temperatures, it is necessary that the diols, triols, and acids are not significant sources of ethanol. This is achieved by postulating that the compounds with multiple hydroxy groups preferentially elimi-

nate water and form the silicate or acid. The final adjustment involves preferential decomposition of the acid to give ethylene rather than ethanol. This is rationalized in terms of the retro-ene reaction, which is postulated to be much faster than the four-center process leading to ethanol (see Mechanisms section of the Discussion). On this basis the experimental data can be fitted with good accuracy. Although decomposition of ethanol itself is included in the model, this reaction is too slow to substantially affect the ethanol concentration even at the highest temperatures.

By paring out those reactions that make a minimal contribution to the product flux, an essentially equally good fit could be made with a smaller set of reactions. However, since identical rate parameters have been assigned for similar reactions, we believe it is more proper to consider the larger set. It is essential to recognize that the data set given in Table 3 is not unique and that the assigned rate parameters for some of the reactions have little effect on the model. Because of this, much care should be exercised in the use of some portions of the data base in other applications.

As a check of the initial stages of reaction, a model of DMDEOS decomposition was also constructed. Because DMDEOS has only two ethoxy groups, this is a much simpler system and the overall reaction can be represented by many fewer reactions than for TEOS. Using the rate parameters of Table 3 for the analogous reactions, we obtain the lines in Figure 3. As shown, the product yields per destroyed DMDEOS are in reasonable accord with the measurements. Exact agreement is not expected since the methyl for ethoxy substitution should lead to some variation in the rate constants.

Probably the most serious problem in the reaction scheme given here is the low activation energy for the ethanol formation process in the decomposition of the silanol. As mentioned earlier, the thermodynamics of Ho and Melius leads to a reaction endothermicity of 292 kJ/mol. Our activation energy is less

TABLE 4: Rate Constants Used in Reproducting Results in Figure 2, Assuming Ethanol Is Not Formed in the High-Temperature Regime

reaction	$\log A$ (s^{-1})	E/R (K^{-1})
$Si(OC_2H_5)_4(TEOS) \rightarrow C_2H_4 + Si(OC_2H_5)_3OH$ (silanol)	15.3	34 500
$Si(OC_2H_5)_4(TEOS) \rightarrow CH_3 + CH_2OSi(OC_2H_5)_3$	17.6	43 300
$Si(OC_2H_5)_3OH$ (silanol) $\rightarrow C_2H_4 + Si(OC_2H_5)_2(OH)_2$ (diol)	15.2	33 600
$Si(OC_2H_5)_3OH$ (silanol) $\rightarrow CH_3 + CH_2OSi(OC_2H_5)_2OH$	17.5	43 300
$Si(OC_2H_5)_2(OH)_2$ (diol) $\rightarrow C_2H_4 + Si(OC_2H_5)(OH)_3$ (triol)	15.0	33 600
$Si(OC_2H_5)_2(OH)_2$ (diol) $\rightarrow CH_3 + CH_2OSi(OC_2H_5)(OH)_2$	17.3	43 300
$Si(OC_2H_5)(OH)_3$ (triol) $\rightarrow C_2H_4 + Si(OH)_4$	14.7	33 600
$Si(OC_2H_5)(OH)_3$ (triol) $\rightarrow CH_3 + CH_2OSi(OH)_3$	17.0	43 300
$CH_2OSi(OC_2H_5)_3 \rightarrow CH_3OSi(OC_2H_5)_2(OC_2H_3) + H$	fast	
$CH_2OSi(OC_2H_5)_2OH \rightarrow CH_3OSi(OC_2H_5)(OC_2H_3)OH + H$	fast	
$CH_2OSi(OC_2H_5)(OH)_2 \rightarrow CH_3OSi(OC_2H_3)(OH)_2 + H$	fast	
$CH_3OSi(OC_2H_5)_2(OC_2H_3) \rightarrow C_2H_4 + CH_3OSi(OC_2H_5)(OC_2H_3)OH$	15.0	33 600
$CH_3OSi(OC_2H_5)_2(OC_2H_3) \rightarrow CH_3 + CH_2OSi(OC_2H_5)(OC_2H_3)(OCH_3)$	17.3	43 300
$CH_2OSi(OC_2H_5)(OC_2H_3)(OCH_3) \rightarrow Si(OCH_3)_2(C_2H_3)_2 + H$	fast	
$CH_3OSi(OC_2H_5)(OC_2H_3)OH \rightarrow C_2H_4 + CH_3OSi(OC_2H_3)(OH)_2$	15.0	33 600
$CH_3OSi(OC_2H_5)(OC_2H_3)OH \rightarrow CH_3 + CH_2OSi(OCH_3)(OC_2H_3)OH$	17.0	43 300
$C_2H_5OH \rightarrow C_2H_4 + H_2O$	13.8	33 300
$C_2H_5OH \rightarrow CH_3 + OH$	16.0	41 800

than 200 kJ/mol. In order to attain rates compatible with their thermochemistry, the A-factor would have to attain values in excess of 10^{16} s^{-1}. This is incompatible with the tight transition state that must be characteristic of this reaction. The high activation energy would also decrease the agreement with the experiments in terms of the temperature dependence. Note that since this is a thermodynamic barrier simple catalysis cannot be an explanation. Instead there would have to be a very complex mechanism or one that has not yet been thought of to account for the observed ethanol formation.

Models with No Gas Phase Ethanol Formation. As a final test of a possible surface mechanism for ethanol formation, we have fit the data assuming that there are no gas phase reactions leading to this product. In this model we assume that gas phase reactions generate the observed ethylene while the ethanol is formed after the shock in some unknown process. The rate expressions needed to fit the data are given in Table 4 and the results plotted in Figure 2. It can be seen that for TEOS an equally good fit can be obtained. It is interesting that this can only be achieved by making the rate constants for the elimination of ethylene from the silanol, the diol, and the triol somewhat larger than the initial elimination of ethylene from TEOS. However, if we then try to fit the DMDEOS data using these same rate constants, Figure 3 shows that the model predicts yields of ethylene that are considerably larger than observed. Further, the predicted increase in ethylene production is much more rapid than observed. The reason is essentially that this model has no rapid gas phase routes for reaction of the silanol other than further elimination of ethylene. Fitting the data would require either the introduction of a competitive reaction or that ethylene elimination from the ethoxy silanol be substantially slower than that from DMDEOS. Since little variation in the per-site elimination rate was observed in the series TEOS, DMDEOS, TMEOS, this latter explanation would seem unlikely. No such difficulties are encountered in the model assuming a purely gas phase mechanism. At present, therefore, we favor the interpretation that gas phase processes are responsible for ethanol production. Finally, note that the mechanisms with or without gas phase ethanol formation require different stable intermediates. Thus these possibilities can be subjected to experimental verification as methods are developed for trapping or detecting these species.

Summary

The primary initial unimolecular process in the gas phase decomposition of TEOS and related ethoxy silicon compounds is shown be a molecular elimination reaction to produce ethylene and the corresponding silanol. A smaller contribution from C−C bond cleavage is also present. Subsequent processes are responsible for ethanol formation, and a general model of the secondary decomposition chemistry has been developed on the basis of the observed product distributions. This model suggests that the initial silanol product is more stable than its carbon analog but still decomposes in the gas phase under our conditions. Two molecular channels, the elimination of ethylene and ethanol, are suggested to be important. Diethoxysilicate is postulated to be an important intermediate and its decomposition results in the formation of additional ethylenes. Our model requires rate parameters for the formation of ethanol and water that are incompatible with the calculated thermodynamics of Ho and Melius.

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