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Kinetics and Thermochemistry of Tetramethyl and Tetraethyl Orthosilicates in the Gas Phase

by

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Introduction

Recently there has been considerable interest in the chemistry of tetraalkyl orthosilicates, particularly with respect to the deposition of SiO_2 insulating films using tetraethyl orthosilicate and other larger members of the homolog.[1-8] Most of these studies were carried out on solid surfaces and often involved the interaction of various silicate molecules with hydroxyl groups on the surface.[9,10]

To date, very little information is available on the thermochemistry and the stabilities of the whole class of $Si(OR)_4$ molecules, where R = alkyl. For example, what is the strength of the RO-$Si(OR)_3$ or the R-$OSi(OR)_3$ bond? To our knowledge, no such information is available in the literature today.

In order to understand the basic thermochemistry of the $Si(OR)_4$ molecules, we have recently investigated the kinetics of thermal decomposition of tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) in the gas phase by Fourier transform infrared spectrometry. Time-resolved concentration profiles of the reactants and major products were measured as functions of temperature and the partial pressure of the reactants. The preliminary results of this study[11] indicate that TMOS decays with an apparent global first-order rate constant, $k_g = 1.4\times10^{16} \exp(-81{,}200/RT)$ s^{-1}, which differs considerably from that for TEOS, $k_g = 7.4\times10^{10} \exp(-49{,}500/RT)$ s^{-1}; where R = 1.987 cal/mole.deg. At 800 K, TMOS is 2400 times more stable than TEOS. This result clearly suggests that TEOS, which possesses β-hydrogens, is capable of undergoing a molecular elimination reaction producing C_2H_4, and other stable intermediates. Such a low-energy reaction path, on the other hand, is not available for TMOS.[11]

To fully elucidate the mechanism of the TMOS decomposition reaction as well as to determine the amount of energy required to break the C-O or the Si-O bond as mentioned above, we have carried out additional kinetic measurements using toluene as a radical scavenger. These new and earlier kinetic data have been kinetically modeled using a comprehensive set of reactions based on the thermochemical data predicted by the BAC-MP4 (bond-additivity-corrected Møller-Plesset 4th order perturbation) method.[12,13] The results of this new study reported herein reveal for the first time the intricate and fascinating fragmentation chemistry of TMOS, which is much different from that of TEOS and other tetraalkyl orthosilicates containing β-hydrogens.

Results and Conclusions

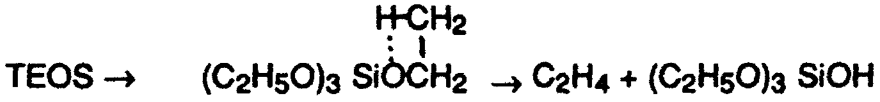
The thermal decomposition of $Si(OCH_3)_4$ (TMOS) and $Si(OC_2H_5)_4$ (TEOS) have been studied by FTIR in the temperature ranges 858-988 K and 780-820 K, respectively. The experiment was carried out in a static cell at constant pressure of 700 torr under highly diluted conditions. Additional experiments were performed by using toluene as a radical scavenger. The species monitored in the TMOS system included TMOS, CH_2O, CH_4 and CO, while in the TEOS system, C_2H_4, CH_3CHO, CO and TEOS were monitored. According to these measurements, the first-order global rate constants for the disappearance of TMOS without and with toluene can be given by $k_g = 1.4 \times 10^{16} \exp(-81{,}300/RT)\ s^{-1}$ and $k_g = 2.0 \times 10^{14} \exp(-74{,}500/RT)\ s^{-1}$, respectively. The noticeable difference between the two sets of Arrhenius parameters suggests that, in the absence of the inhibitor, the reactant was consumed to a significant extent by radical attacks at higher temperatures. The experimental data were kinetically modeled with the aid of a quantum-chemical calculation using the BAC-MP4 method.[12,13] The results of the kinetic modeling, using the mechanism constructed on the basis of the quantum-chemical data (see Tables I and II) and the known C/H/O chemistry, identified two rate-controlling reactions:

(2) $TMOS \rightarrow CH_3OH + (CH_3O)_2SiOCH_2$

(3) $CH_2OSi(OCH_3)_3 \rightarrow CH_2O + Si(OCH_3)_3$

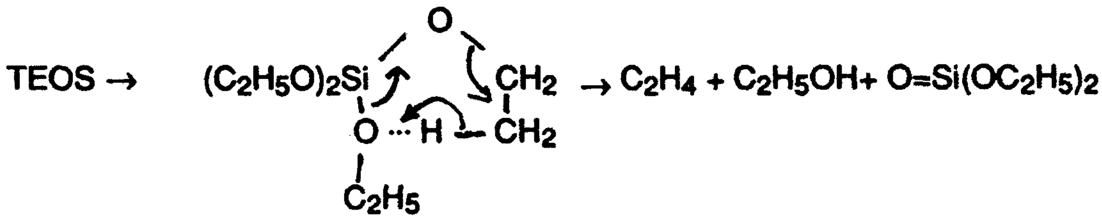
which have the following respective first-order rate constants, given in the unit of s^{-1}: $k_2 = 1.6 \times 10^{14} \exp(-74{,}000/RT)$ and $k_3 = 3.8 \times 10^{14} \exp(-60{,}000/RT)$.

A similar analysis for the TEOS system on the basis of the thermochemical data provided by the BAC-MP4 quantum calculation led us to conclude that the reaction occurs mainly by the four-centered elimination mechanism:

(4)


$$\mathrm{TEOS} \rightarrow (C_2H_5O)_3\,Si\overset{H-CH_2}{\overset{\vdots\ \ |}{OCH_2}} \rightarrow C_2H_4 + (C_2H_5O)_3\,SiOH$$

The six-centered elimination reaction:

(5)


$$\mathrm{TEOS} \rightarrow (C_2H_5O)_2Si(OC_2H_5)(OCH_2CH_2\cdots H) \rightarrow C_2H_4 + C_2H_5OH + O{=}Si(OC_2H_5)_2$$

is 80 kcal/mole more endothermic than the four-centered elimination reaction shown above, whose decomposition rate constant has been evaluated to be $k_4 = 5.0 \times 10^{13} \exp(-61{,}500/RT)\,s^{-1}$.

The thermochemical data summarized in Tables I and II provide for the first time the much needed heats of formation and bond energy information for the $SiO_xC_yH_z$ species.

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References

(1) Sherman, A. *Chemical Vapor Deposition for Microelectronics*, Noyes Publication, Park Ridge, New Jersey, **1987**.

(2) Sze, S.M. *Physics of Semiconductor Surface*, 2nd Ed. John Wiley and Sons, New York, 1981.

(3) Atkinson, A. *Rep. Prog. Phys.* **1985,** 37, 231 .

(4) Irene, E.A. *CRC Critical Reviews in Solid State and Material Science*, **1988,** 14, 175 .

(5) Becker, F.S.; Pawlik, D.; Anzinger, H.; Spitzer, A. *J. Vac. Sci. Technol.* **1987,** B5, 1555 .

(6) Adams, A.C.; Capio, C.D. *J. Electrochem. Soc.* **1979**, 126, 1042

(7) Desu, S.B. *J. Am. Ceram. Soc.* **1989**, 72, 1615 .

(8) Raupp, G.B.; Shemansky, F.A.; Cale, T.S. *J. Vac. Sci. Technol.* B, in press.

(9) Hertl, W. *J. Phys. Chem.* **1968**, 72, 1248.

(10) Hertl, W. *J. Phys. Chem.* **1968**, 72, 3993

(11) Chu, J.C.S.; Breslin, J.; Wang, N.S.; Lin, M.C. *Mater. Letts.* **1991**, 12, 179.

(12) Melius, C.F.; Binkley, J.S. *20th Symp. (Intern.) on Combust.*, The Combustion Institute, **1984**, p.575.

TABLE I. Energetics of species relevant to the present system calculated by the BAC-MP4 method.

Species	$\Delta H^{o}_{f,0}$ (Kcal/mol) ± Estimated Uncertainty
$Si(OH)_3OCH_3$	-300.5 ± 5.5
$Si(OH)_3$	-180.0 ± 4.4
$OSi(OCH_3)_2$	-160.0 ± 7.1
$CH_2OSi(OH)_3$	-255.7 ± 5.5
CH_3OSiO_2	-96.2 ± 7.6
$Si(OH)_2OCH_3$	-169.6 ± 4.2
$Si(OH)(OCH_3)_2$	-159.6 ± 4.0
$Si(OH)_2(OCH_3)_2$	-288.0 ± 5.3
$C_2H_5OSi(OH)_3$	-307.5 ± 5.6
c-$Si(OH)_2OCH_2$-	-178.7 ± 5.0
SiH_2OH	-21.5 ± 1.9
H_2SiO	-16.5 ± 8.2
$OSi(OH)_2$	-177.9 ± 7.3
$SiH(OH)_2$	-99.3 ± 3.2
$SiH(OH)_2O$	-155.4 ± 4.3
$SiH_2(OH)_2$	-143.7 ± 3.1
$SiH(OH)_3$	-277.3 ± 4.3
$Si(OH)_4$	-311.0 ± 5.7
$HOSiO_2$	-106.2 ± 7.7
HSiOH	-18.5 ± 3.0
$Si(OH)_3O$	-238.4 ± 5.7
H_3SiOH	-62.1 ± 1.7
$Si(OH)_2$	-36.3 ± 4.3
$OSi(OH)(OCH_3)$	-170.6 ± 7.2
SiO_2	-54.4 ± 9.9
CH_3OH	-46.2
CH_3O	7.7 ± 1.3
CH_2OH	-3.2 ± 1.1
CH_3	35.6 ± 1.2
CH_2O	-25.9 ± 1.0
CH_2	102.7 ± 3.9
OH	9.5 ± 1.0
H	52.7
O	59.4

Table II. Dissociation energies of relevant chemical bonds based on the heats of formation given in Table I.

Dissociating Bond	BDE (Kcal/mol)
1. $H--CH_2OSi(OH)_3$	96.9
2. $CH_3--OSi(OH)_3$	97.7
3. $CH_3O--Si(OH)_3$	128.2
4. $H--OSi(OH)_3$	124.7
5. $HO--Si(OH)_3$	140.5
6. $O--Si(OH)_3$	117.4
7 $CH_2--OSi(OH)_3$	120.0
8. $CH_2O--Si(OH)_3$	49.8
9. $CH_3--OSi(OH)_2$	25.5
10. $CH_3O--Si(OH)_2$	141.0
11. $CH_3O--(CH_3O)Si(OH)_2$	126.1
12. $HO--(OH)Si(OCH_3)_2$	137.9
13. $H--OSi(O)(OH)$	125.8
14. $CH_3--CH_2OSi(OH)_3$	87.4
15. $C_2H_5--OSi(OH)_3$	100.6
16. CH_3--OH	91.3
17. $H--CH_2OH$	95.7