J. Am. Chem. Soc. **1998,** *120,* 1552−1555

The Catalyzed Hydrosilation Reaction

Brett M. Bode, Paul N. Day,[†] and Mark S. Gordon*

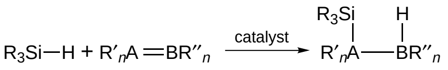
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received September 2, 1997. Revised Manuscript Received December 12, 1997

Abstract: *Ab initio* electronic structure calculations with RHF, MP2, and CCSD(T) wave functions have been used to investigate a reaction path for the hydrosilation reaction catalyzed by divalent titanium (modeled by TiH_2). Optimized structures and energies are presented. All levels of theory predict a barrierless reaction path compared to a barrier of 78 kcal/mol for the uncatalyzed reaction. The use of correlated wave functions (MP2 or CCSD(T)) is required to obtain accurate structures and energies.

I. Introduction

The hydrosilation reaction is a general method of adding an $Si-H$ bond across a $C-C$ double bond. This method encompasses a wide variety of substituted alkenes, dienes, and alkynes leading to many different organosilicon products. Thus the method is very useful; indeed it is the second most important method of producing organosilanes on a large scale.[1] The general hydrosilation reaction may be written as:



$$R_3Si{-}H + R'_nA{=}BR''_n \xrightarrow{\text{catalyst}} R'_n\overset{R_3Si}{A}{-}\overset{H}{B}R''_n$$

One of the simplest examples known experimentally is the addition of trichlorosilane to ethylene, which will occur rapidly at room temperature and give nearly 100% yields with a variety of homogeneous transition metal based catalysts.[2]

Several analogous uncatalyzed reactions ($HSiCl_3$, SiH_4 + ethylene, SiH_4 + propene) were studied previously;[3] all were found to have large (≥54 kcal/mol) barriers. Thus, the catalyst is crucial in making the process economically viable. Industrially one active catalyst is believed to be a divalent Cp_2Ti species ($Cp = C_5H_5$).[1] The role of Cp_2Ti in catalyzing the polymerization of primary organosilanes has been studied by Harrod *et al.*[4] These calculations suggest that Cp_2Ti exhibits a strong catalytic effect, but due to the size of the catalyst only selected points along the reaction path were studied in detail by using double-ζ and triple-ζ quality basis sets and density functional theory. The nature of the bridging interactions between Ti and C in $Ti(C(Si(CH_3)_3){=}C(C_6H_5)(CH_3))(Cp)^+{}_2$, an intermediate in a Ziegler catalyst system, has also been examined. The computed structure matched the experimental structure very well, even though the calculations employed fairly low levels of theory (RHF wave functions with a 3-21G basis set).[5]

There have been several recent studies on similar catalysts. A study of a silylene-bridged Cp_2Ti and its role in ethylene polymerization[6] employed RHF, MP2, and QCISD calculations with small basis sets (effective core potentials on the metal and 3-21G on the carbons and hydrogens). The results give a qualitative picture of the reaction path and several important structures along it, but the entire path was not examined. The Ziegler−Natta olefin polymerization process has been studied by several groups interested in the role of the $TiCl_2$ catalyst.[7−9] While these studies do provide a qualitative picture of the process, they all use relatively small basis sets and modest levels of theory (RHF and MP2).

This paper will consider the simplest prototypical example of a catalyzed hydrosilation reaction, in which A and B are carbon; R, R′ and R″ are hydrogen; and the catalyst is TiH_2. The choice of reactants and catalyst allows mapping the entire reaction path at a high level of theory. Particularly, the choice of TiH_2 as the catalyst allows the use of high-level all-electron *ab inito* wave functions which would not be possible if the more complex catalysts such as $TiCl_2$ or $TiCp_2$ were used. Clearly, subsequent calculations will need to address the steric and electronic effects introduced by the Cl and Cp substituents. Nonetheless, TiH_2 provides an important baseline for comparison.

II. Computational Methods

The minimum energy reaction path connecting reactants to products was determined by using all electron *ab initio* wave functions. The basis set used was a triple-ζ quality valance[10] plus 1 d-type polarization function on C, Si and 1 p-type polarization function on the hydrogens.[11]

The reaction path was determined by first optimizing the structures of the minima and transition states (TS) by using analytic gradients and a modified Newton−Raphson algorithm. Each stationary point

---

[†] Present address: WL/MLPJ Building 651, 3005 P St. Ste. 1, Wright-Patterson, AFB, OH 45433.

(1) Barton, T. J.; Boudjouck, P. Organosilicon chemistry−a brief overview. In *Advances in Silicon-Based Polymer Science*; Advances in Chemistry Series No. 224; Ziegler J., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; pp 3−46.

(2) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407−447.

(3) Day, P. N.; Gordon, M. S. *Theor. Chim. Acta* **1995**, *91*, 83−90.

(4) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897−902.

(5) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108−112.

(6) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746−758.

(7) Jensen, V. R.; Børve, K. J.; Ystenes, M. *J. Am. Chem. Soc.* **1995**, *117*, 4109−4117.

(8) Sakai, S. *J. Phys. Chem.* **1994**, *98*, 12053−12058.

(9) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, *114*, 2359−2366.

(10) For H, C: Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716−723. For Si: McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639−5648. For Ti: Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033−1036. This has been extended to triple-ζ quality by using d functions (developed by: Rappe, A. K.; Smedley, T. A.; Goddard, W. A., III *J. Phys. Chem.* **1981**, *85*, 2607−2611), deleting Wachters' most diffuse s function $\zeta = 0.0333$, adding an s function with $\zeta = 0.209$ to better describe the 3s−4s region, and adding two p functions $\zeta = 0.1506$ and 0.0611 to allow for a 4p.

(11) The exponents used were as follows: H $\zeta_p = 1.0$; C $\zeta_d = 0.72$; Si $\zeta_d = 0.388$.

S0002-7863(97)03072-2 CCC: $15.00

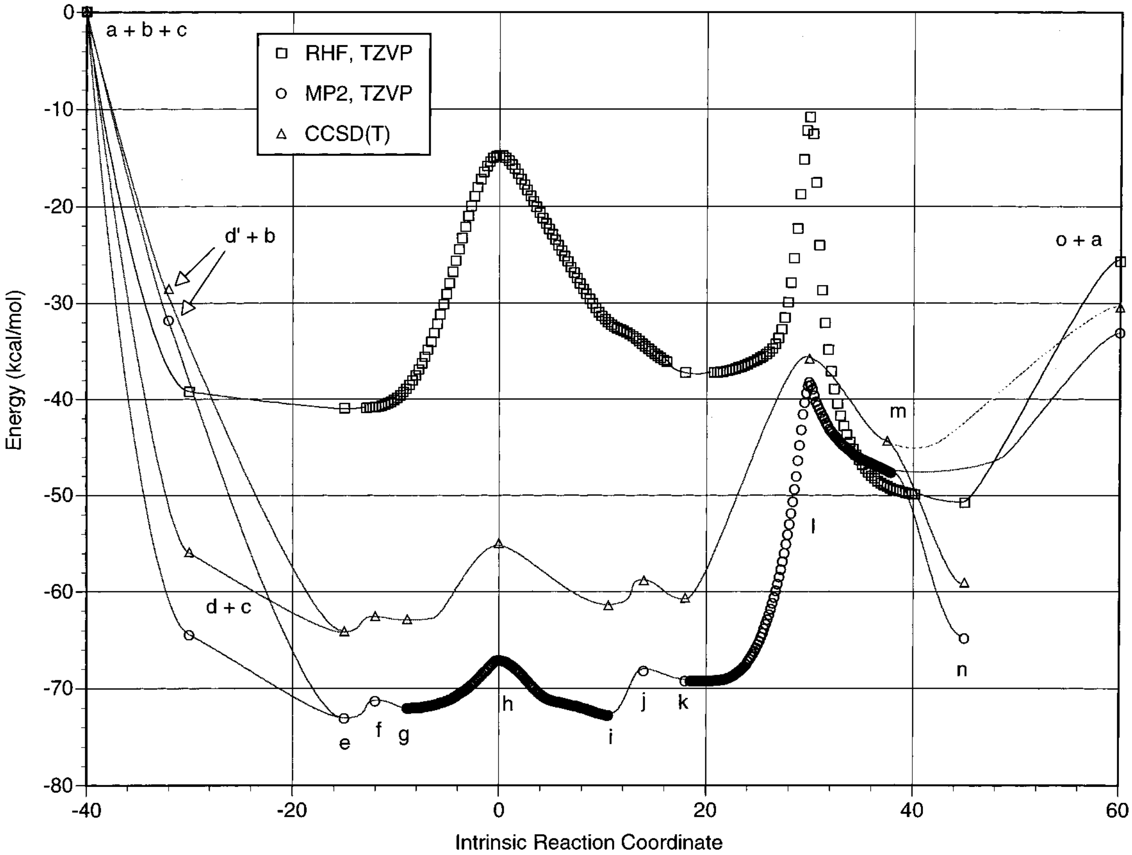


Figure 1. RHF, MP2, and CCSD(T) energies.

was confirmed by computing the matrix of energy second derivatives, or Hessian, to obtain the harmonic normal modes and corresponding frequencies (each minimum has zero and each transition state has one imaginary mode). The calculated frequencies were also used to obtain the harmonic zero-point energies used to convert energy differences to 0 K enthalpy differences. Finally the path connecting each TS to the nearest minima on each side of the TS was computed by using the Gonzalez-Schlegel second-order intrinsic reaction coordinate path (IRC) method[12] with a step size of 0.3 amu$^{1/2}$•bohr for the first TS and 0.05 amu$^{1/2}$•bohr for the second TS.

The path was initially optimized at the restricted Hartree−Fock (RHF) level of theory, then refined by using Møller−Plesset second-order perturbation theory (MP2). Single-point energies were computed at the MP2 optimized stationary points by using coupled cluster singles and doubles plus perturbative triples (CCSD(T)).

The GAMESS[13] program was used for all of the RHF calculations and a portion of the MP2 optimizations. The Gaussian 92 suite of programs[14] was used for the remainder of the MP2 calculations and the CCSD(T) calculations.

III. Results and Discussion

Figure 1 shows the energy profile of the proposed catalyzed reaction. The zero of energy on the curve for each level of theory is the sum of the reactant energies at that level of theory (structures **a**, **b**, and **c** in Figure 2). The MP2 structures at each stationary point are given in Figure 2.[15] The MP2 and CCSD(T) total energies and the MP2 vibrational zero point energy (ZPE) corrections for each geometry point marked in Figures 1 and 2 are available as Supporting Information. MP2 and CCSD(T) ZPE corrected energies are listed relative to the zero of energy in Table 1.

It is important to note that all points on the energy plot in Figure 1 lie below the energy of the reactants, in contrast to the large barrier in the uncatalyzed reaction. Note also that there are large differences between the SCF and MP2 energy profiles, while the differences between MP2 and CCSD(T) are much smaller. So, electron correlation is essential for a correct description of this reaction surface, and MP2 is qualitatively correct.

There are two possibilities for the first step of the reaction, both of which are barrierless processes. The first, and more exothermic, is to add the TiH_2 catalyst across the ethylene double bond to form the three-membered-ring compound shown in Figure 2d. This process is downhill in energy by 61.9 (53.4) kcal/mol at the ZPE corrected MP2 (CCSD(T)) level of theory. Note that, based on the large exothermicity and the large (0.016 Å) increase in the CC bond length, structure **d** is a three-membered ring, not a π complex. Silane will then add to form the complex depicted in Figure 2e. This second barrierless addition is downhill by 6.5 (6.0) kcal/mol.

The electronic structure of TiH_2 was considered in detail previously.[16] Like CH_2, the ground state is a triplet, and the

---

[12] (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523−5527. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853−5860.

[13] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. The general atomic and molecular electronic structure system. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

[14] Gaussian 92 rev C, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogie, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. L.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Pople, J. A.; Gaussian Inc.: Pittsburgh, PA, 1992.

[15] The full set of Cartesian coordinates for each structure available as Supporting Information as well as on the following WWW site: http://www.msg.ameslab.gov/.

[16] Kudo, T.; Gordon, M. S. *J. Chem. Phys.* **1995**, *102*, 6806−6811.

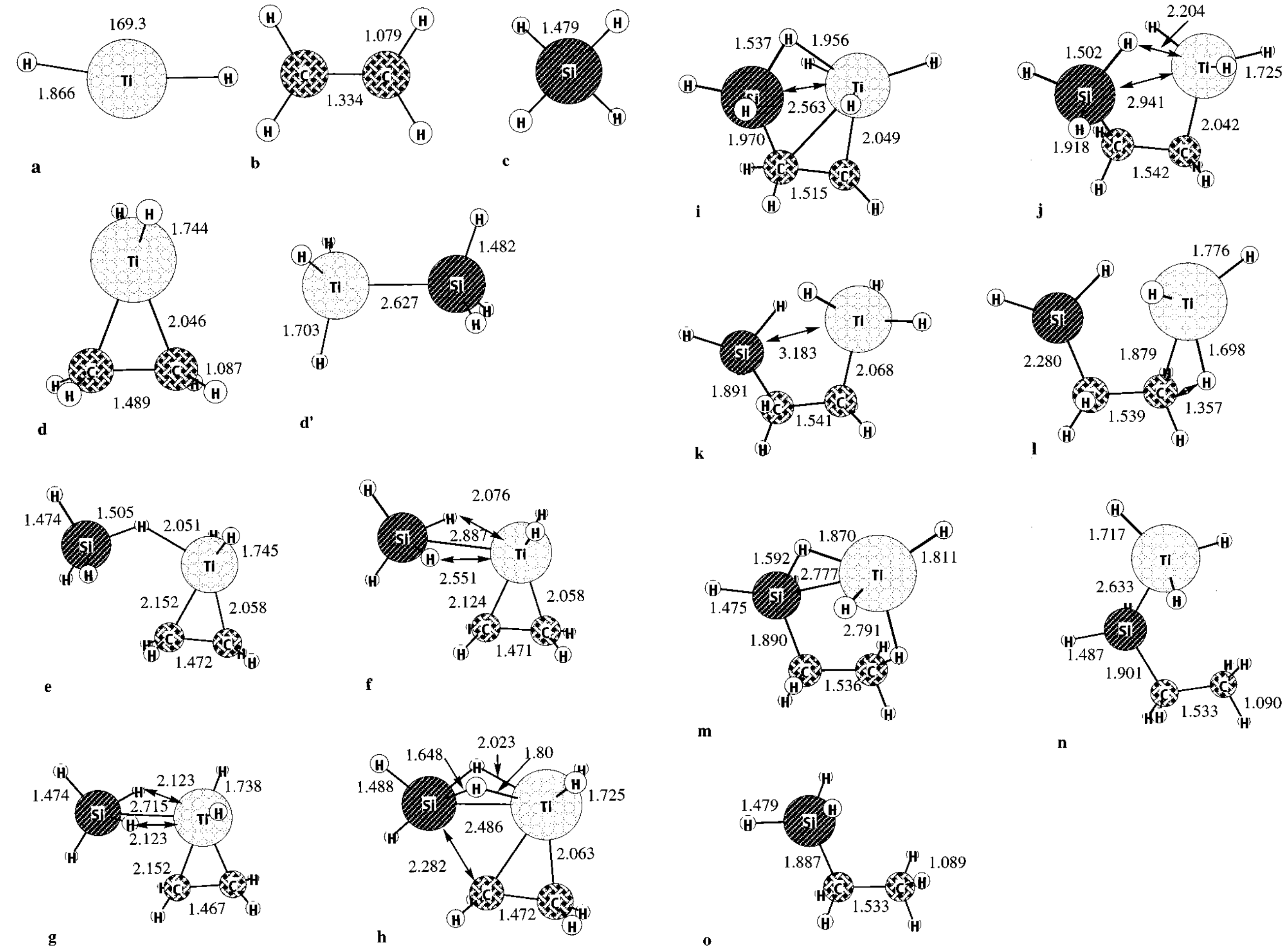


Figure 2. MP2 structures along the minimum energy reaction path.

Table 1. MP2 and CCSD(T) Relative Energies (kcal/mol) with ZPE Correction

geometry point	MP2 + MP2 ZPE	CCSD(T) + MP2 ZPE
$a + b + c$ (reactants)	0	0
$d' + b$	−31.1	−27.8
$d + c$	−61.9	−53.4
e	−68.4	−59.4
f	−66.6	−57.8
g	−66.6	−57.4
h	−61.3	−49.2
i	−67.2	−55.8
j	−64.0	−54.6
k	−65.4	−56.8
l	−33.5	−31.1
m	−39.0	−37.0
n	−59.2	−53.3
$o + a$ (products)	−28.0	−25.4

lowest singlet state is 21 kcal/mol higher in energy. Since TiH_2 has an electronic structure similar to singlet CH_2 or SiH_2 (s^2d^2 vs s^2p^2), a reasonable expectation is that an alternative mechanism would start with an insertion of TiH_2 into an Si−H bond of silane. Indeed, this occurs with no barrier to produce structure **d′**, a Ti−Si analogue of ethane. This step is downhill by 31.9 (27.8) kcal/mol. When ethylene is added to this compound, it rearranges with no barrier to the same structure as in Figure 2e.

So, whether the TiH_2 catalyst adds to ethylene or silane initially, the net result after the two reactants and the catalyst have been added together is the formation of compound **e**, with no intervening barrier. The overall exothermicity to this point is 68.4 (59.4) kcal/mol. This very large drop in energy drives the entire reaction path down in energy. In fact the reaction path is forced down enough that all subsequent points are below the reactants in energy.

Recall that the final desired product is ethylsilane. So, starting from compound 2e, the silyl group needs to migrate to the nearest (α) carbon, and a hydrogen needs to be transferred to the adjacent (β) carbon, with the ultimate removal of the TiH_2 catalyst. Therefore, the next step in the reaction is to transfer a H from the complexed silane to the Ti and to attach the Si to the α C.

The first part of this step involves rotation of the silane such that there are 2 bridging hydrogens between the Si and Ti; that is e→g via f in Figures 1 and 2. At the MP2 level there is a small barrier (at structure f) of 1.7 kcal/mol to this process, but after the ZPE corrections are added the barrier disappears. The reaction then proceeds through transition state h with a barrier of 5.3 (8.2) kcal/mol, leading to the four-membered ring shown in Figure 2i. This ring is 5.9 (6.6) kcal/mol below the TS h. The four-membered ring can be opened up by breaking the Si−Ti bond to give the compound **k**. The TS for this step is shown in Figure 2j. It has a barrier height of 3.2 (1.2) kcal/mol. Compound **k** is 1.4 (2.1) kcal/mol below the TS j.

The final step in the process is to regenerate the catalyst by transfer of a hydrogen from Ti to C and elimination of TiH_2. The transition state for this process is shown in Figure 2l; the associated barrier height is 31.9 (25.7) kcal/mol. This TS is still 33.5 (31.1) kcal/mol lower in energy than the initial reactants. The IRC from this TS leads to the structure shown in Figure 2m, which is 5.2 (5.9) kcal/mol below the TS. The structure shown in Figure 2m is not a stationary point, but it illustrates that the reaction path goes through a structure in which the TiH_2 is complexed to two hydrogens. Optimization from this point leads to the insertion of TiH_2 into an Si−H bond, as shown in Figure 2n. The insertion product is 25.7 (22.2) kcal/mol below the TS in energy. However, the TiH_2 in Figure 2m is not tightly bound to the ethylsilane as evidenced by both the relatively long Ti−Si and Ti−H bond distances and the fact that it is a modest 11.0 (11.6) kcal/mol in energy below separated products. Thus we do not expect a transition state for the process of simply abstracting the TiH_2 to form separated products. This can occur readily due to the excess energy available to the system, since the separated products are 28.0 (25.4) kcal/mol below the reactants in energy. Note that the *reverse* barriers for elimination of singlet CH_2 from methane and singlet SiH_2 from silane are ca. zero.[17] It is also much less likely that the catalyst will insert when both the catalyst and the silyl group have more bulky substituents such as Cl or Cp rings.

Once TiH_2 is removed, the process is complete with ethylsilane as the product. The overall process is exothermic by 28.0 (25.4) kcal/mol at the ZPE corrected MP2 (CCSD(T)) level of theory. This compares with the value of 29.1 kcal/mol computed by Day and Gordon[3] at the MP2/6-311G(d,p) level of theory and a value of 27.4 kcal/mol computed by McDouall *et al.*[18] at the MP4/6-31G(d)//HF/3-21G level of theory. There does not seem to be a good experimental ΔH_0 for this reaction, but we can estimate the value to be 28.9 kcal/mol based on the experimental heats of formation for ethene and silane,[19] and the best previous theoretical heat of formation for ethylsilane.[20]

The driving force for the entire reaction comes in the first two steps with the formation of the compound shown in Figure 2e, which is 68.4 (59.4) kcal/mol below the reactants in energy and is the global minimum on the reaction surface. The reasons this structure is so stable are illustrated by the first two steps in the reaction. In the first step the electron deficient TiH_2 adds to the ethene across the π bond in much the same manner as the addition of CH_2 to ethylene to form cyclopropane. The second step is much less exothermic and is driven mostly by the electrostatic attraction between the positively charged titanium (+0.83) and the negative hydrogen (−0.12) on the silicon.

IV. Conclusions

The results presented here clearly show that divalent titanium is an effective catalyst for the hydrosilation reaction. Further work, currently in progress, will examine the effect of substitution on catalyst and reactants, but even the simple model catalyst, TiH_2, used here clearly shows strong catalytic behavior. The overall catalyzed reaction has no net barrier, because of the very stable cyclic $TiH_2CH_2CH_2$ intermediate. However, the energy profile of the multistep process (Figure 1) does offer the possibility of finding some of the intermediate structures if the process was carried out at low temperature.

Acknowledgment. The work described in this paper was supported by grants from Iowa State University in the form of a Department of Education GAANN fellowship awarded to B.M.B. and in the form of a grant to purchase computers used in this project, the National Science Foundation (CHE-9633480), and the Air Force Office for Scientific Research (F49-620-95-1-0073). The computations were performed in part on computers provided by Iowa State University and through a grant of computer time at the San Diego Supercomputer Center.

Supporting Information Available: Full set of Cartesian coordinates for each structure (5 pages). See any current masthead page for ordering information and Web access instructions.

JA9730728

---

(17) Gordon, M. S.; Gano, D. R.; Binkley, J. S.; Frisch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2191−2195.

(18) McDouall, J. J. W.; Schlegel, H. B.; Francisco, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 4622−4627.

(19) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data Suppl.* **1982**, *11*, 2.

(20) Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584−1585.