Interaction of Pd and $PdCl_2$ with Cellulose: A Theoretical Investigation

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The pyrolytic fragmentation of cellulose in the presence of atomic palladium (Pd) and palladium(II) chloride ($PdCl_2$) has been studied with use of hybrid density functional theory and cellobiose as a model for cellulose. The configuration changes in the host, rearrangement of geometries of the products, and the respective reaction energetics for different fragmentation pathways are analyzed. While Pd is found to undergo insertion at the β-1,4-linkage oxygen (O1)−carbon (C-1) of the rings, Pd(II) chloride is observed to promote the cleavage of the chain as well as rearrangement of the rings. A detailed mechanism for the formation of levoglucosan from one of the fragments following the interaction with $PdCl_2$ is also highlighted.

I. Introduction

One of the most significant bio-organic degradation processes involves the pyrolysis of cellulose.[1,2] The burning of the forest fuels,[3−5] the pyrolysis of tobacco in cigarettes,[1,2] as well as biodegradation in other branches of forestry invoke processes where the cellulose chains are broken to form a range of products starting from small aliphatic aldehydes, hydroxyaldehydes, alcohols to furan derivatives, polycyclic aromatic hydrocarbons (PAHs), as well as both open chain and cyclic anhydrohexoses. Experimental studies indicate that the nature of the products can be affected by adding salts of selected metals.[6−18] As an example, Heyns et al.[17] have studied the pyrolysis of several carbohydrates, including cellulose, in the presence of added inorganics. They claim that while addition of acid salts has a small effect on the composition of the pyrolysis products, neutral salts have no effect. On the other hand they find that addition of basic salts suppresses the formation of furans and facilitates the formation of carbonyl compounds. Soares et al.[18] used FTIR as well as ^1H and ^{13}C solid-state NMR techniques to study the thermal degradation of cellulose at temperatures ranging from 200 to 550 °C, in the presence of NaCl, $ZnCl_2$, and $CuCl_2$. They concluded that these salts had "little or no effect on the rate or mechanism of degradation". On the contrary, McGrath et al.[8] have concluded that addition of Na, K, and Ca inorganic salts to cellulose increases the "char" yield during pyrolysis, which in turn is thought to increase the yield of PAHs. In pyrolysis of cellulose at 300 °C, Shafizadeh et al.[16] observed that the presence of slight quantities of the Lewis acid $SbCl_3$ decreased the yield of levoglucosan (a typical dehydration product obtained from the thermal degradation of carbohydrates) and increased the formation of glycoaldehyde. NaCl and Na_2CO_3 are also known to have the same effect when present during cellulose pyrolysis. These studies indicate two effects. First, that the nature of degradation and the resulting compounds can be controlled by inserting metal ions. Second, that the valence state of the metal is important since different salts of the same metal lead to different compounds. From a fundamental standpoint, it is then interesting to explore how the presence of metal ions in various valence states can modify or break the cellulose chains. There have been several studies dealing with the interaction of platinum-group metals with carbohydrates[19−21] but a detailed understanding of the mechanisms involved is still lacking. Such an understanding is not only useful to understand the fundamental mechanisms by which the metal atoms incorporate into organic chains but also to control the nature of the products in, e.g., the cigarette industry with the ultimate objective of eliminating the undesirable products.

The purpose of the present work is to carry out such studies. In particular, we focus on the interaction of Pd and $PdCl_2$ with cellulose. Our studies are carried out within a real space density functional approach where the infinite system is modeled by a finite cluster. Here, we have used a cellobiose molecule to model the cellulose. We then present a detailed investigation of the reaction processes and the corresponding barriers via which a celloboise unit leads to the formation of levoglucosan. The paper is organized as follows. In section II we briefly discuss the computational details. In section III we present the results and outline the reactions occurring along with their energetics in detail. Finally, in section IV we present a summary of our results.

II. Computational Details

All the calculations presented in this paper were done with the GAUSSIAN 03 electronic structure program[22] package, using density-functional theory (DFT) with the B3LYP (three-parameter hybrid Becke exchange and Lee−Yang−Parr correlation functional)[23−28] method. For the main group elements, the triple-ζ plus polarization function 6-311G(d,p) basis set consisting of a "d" polarization function on C, O, and Cl and a "p" polarization function on H was used. The Hay−Wadt[29]

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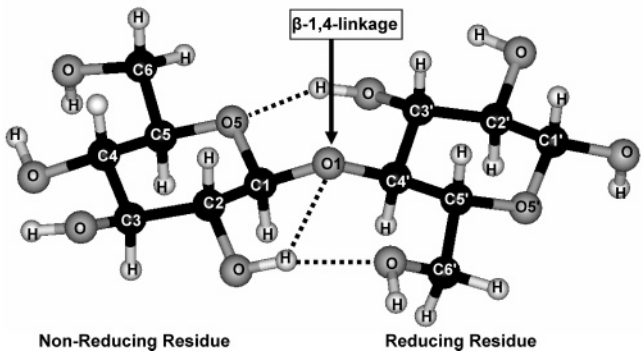

Figure 1. Optimized structure of a cellobiose molecule. The dotted lines represent intramolecular hydrogen bonds. All structural parameters of the cellobiose molecule are given in Table 1.

semirelativistic pseudopotential was used to represent the core electrons of Pd and the associated basis sets were also used to describe the valence shell. To simulate harsh reaction conditions, as in pyrolysis, where a huge amount of energy is available to the reacting system, we have often placed reactants in extreme close proximity (unphysical bonding distances) to each other, such that the reacting system is placed at a much higher energy on the potential energy surface than actual reactants are at room temperature (under milder reaction conditions), thus ensuring that the energy barriers are crossed. In the geometry optimization procedures employed here, the convergence criteria for the energy and its gradient are set to an order of 10^{-9} and 10^{-4} atomic units, respectively. The nature of any proposed reaction intermediate as opposed to transition state species, used to elucidate any reaction mechanism, was verified by subsequent harmonic frequency calculations, which also yielded zero-point energy corrections.

III. Results and Discussions

This section is further divided into three subsections. Subsection 1 deals with a description of the cellobiose unit that we have used to model the polymeric cellulose chain. Subsections 2 and 3 deal with the interaction of atomic Pd and $PdCl_2$ with cellobiose (cellulose) unit, respectively.

(1) Cellobiose. As mentioned before, in our studies of modeling the interaction of cellulose in the presence of added inorganics, we consider a single cellobiose unit. Cellobiose (see Figure 1) is the smallest repeating unit of cellulose comprised of two D-glucose units linked by an oxygen atom (O1) in what is known as a β-1,4-linkage. In other words the first carbon (C-1) of one unit is linked equatorially to the fourth carbon (C4′) of the other by a linkage oxygen atom. Figure 1 shows the equilibrium geometry and Table 1 lists the structural parameters of a cellobiose molecule as obtained from our calculations. All the bond lengths, shown in Table 1, are typical of a single bond (C−C, C−O, C−H, and O−H) between the respective atoms in the molecule. In addition, we also show the three intramolecular hydrogen bonds in Figure 1 as dotted lines. Nishiyama et al.[30,31] have obtained the values for hydrogen bonds in bulk cellulose crystals by synchrotron X-ray and neutron fiber diffraction experiments (shown in parentheses in Table 1). Our values are in very good agreement with the above and the deviations from the experimental numbers range from 1% to 7%. Hence our model of cellobiose is essentially a realistic representation of the local stereochemistry of cellulose in the bulk crystal/polymeric chain. For further discussion we will follow the numbering of the atoms as given in Figure 1, where numbers on the left-hand-side ring (nonreducing residue) are unprimed while the numbers on the right-hand-side ring (reducing residue) are primed′.

TABLE 1: Structural Parameters of Cellobiose As Obtained from the Calculations[a]

β-1,4-O1−C1	1.39	β-1,4-O1−C4′	1.43
O5−C1	1.44	O5′−C1′	1.44
C1−C2	1.53	C1′−C2′	1.53
C2−C3	1.52	C2′−C3′	1.53
C3−C4	1.53	C3′−C4′	1.53
C4−C5	1.54	C4′−C5′	1.54
C5−C6	1.53	C5′−C6′	1.53
C5−O5	1.43	C5′−O5′	1.43
C1−H	1.10	C1′−O(H)	1.38
C2−O(H)	1.41	C1′−H	1.10
C2−H	1.10	C2′−O(H)	1.41
C3−O(H)	1.42	C2′−H	1.10
C3−H	1.10	C3′−O(H)	1.42
C4−O(H)	1.42	C3′−H	1.10
C4−H	1.10	C4′−H	1.10
C5−H	1.10	C5′−H	1.10
C6−H	1.09/1.10	C6′−H	1.09/1.10
C6−O(H)	1.43	C6′−O(H)	1.43
(C2)O−H	0.97	(C1′)O−H	0.96
(C3)O−H	0.97	(C2′)O−H	0.97
(C4)O−H	0.97	(C3′)O−H	0.97
(C6)O−H	0.96	(C6′)O−H	0.96
C1−β-1,4-O1−C4′	119°		
intramolecular H bonds			
O5−H(O−C3′)	1.93 (1.966)[b]		
β-1,4-O1−H(O−C2)	2.45 (2.304)		
(C2−O)H−O−C6′	1.93 (1.832)		

[a] All distances are given in Å. [b] Experimental values are given in parentheses.

(2) Interaction of Atomic Pd with Cellobiose. In this section, we consider the interaction of Pd atom with the cellobiose unit as mentioned above. It is often observed that bulk metals do not affect reactions with organic substrates. Our attempt here is to understand if Pd in its neutral monatomic state interacts with a cellobiose unit. Atomic Pd(0) has a singlet ($^1S_0$; $4d^{10}$) ground electronic state. In the cyclic structure of carbohydrates, it is well-known that the bonds between the ring oxygen atoms (O5/O5′) and the adjacent carbons are very reactive. In the cellobiose unit, we also have another type of C−O bond, namely the ring carbon−β-1,4-linkage oxygen bond ((C-1)−O1−C4′). Perspective attachment of Pd on all these sites is systematically examined to identify the most reactive site in the moiety as well as to provide information for a subsequent study with palladium(II) chloride ($PdCl_2$). The preferential positions of the Pd atom have been investigated by allowing Pd to approach the celloboise molecule from different directions. These include the following: approach of the Pd atom toward the bond between C1′ and O5′, and in the region where it can approach either the bonds between C-1 and β-1,4-O1 or the one between the ring oxygen, O-5, and C-1 of the cellobiose moiety (see Figure 1).

Pd is observed to insert into the bond between O5′ and C1′. This inserted product (see Figure 2a) has a binding energy of ∼0.20 eV (∼4.61 kcal mol^{-1}). The geometry of the ring on the right-hand side is distorted completely with the Pd−O5′, C1′−Pd, and C5′−O5′ distances being 2.00, 1.97, and 1.40 Å, respectively. This product can be viewed as modeling the binding of Pd to a terminal unit of cellulose.

As above, we also find that Pd inserts into the (C-1)−O1 bond. This inserted product (see Figure 2b) is thermodynamically much more stable than the previous inserted product, with a binding energy of ∼0.5 eV (∼11.53 kcal mol^{-1}). The Pd−O1 and the Pd−(C-1) distances are 2.07 and 1.97 Å, respec-

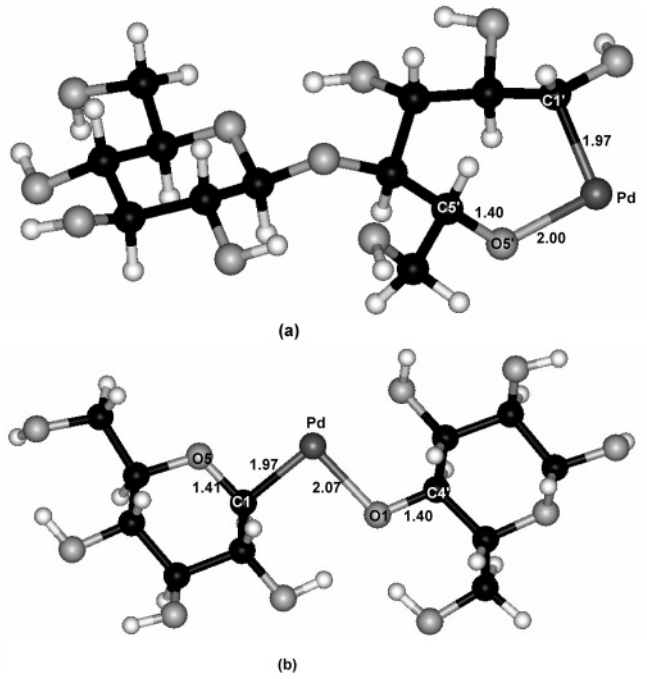

Figure 2. The Pd-inserted products of cellobiose.

tively. Relative to each other the two rings undergo some amount of torsion (one cannot report a torsional angle as the rings are nonplanar) as this Pd-inserted product is formed. In other words, as we observed here, the bond between the anomeric carbon (C-1) and the O1 atom is more vulnerable to attack by added Pd/Pd salts than the other C−O bonds present in the cellobiose unit. Furthermore, we find that the Pd preferred to attack/insert at the (C-1)−O1 linkage site in comparison to the O5−(C-1) bond in the left-hand-side ring of the cellobiose unit. We analyzed the Mulliken charges on the O atoms, the charge density distribution (at several isosurface values), as well as the HOMO/LUMO to understand why Pd prefers to attach to the (C-1)−O1 bond. No clear differences in the electronic structure were found. Thus, we conclude that the probable reason for this insertion to the (C-1)−O1 bond is steric in nature as the O1 site has a more "open" structure.

(3) Interaction of Palladium(II) Chloride and Cellobiose. In this section we describe the interaction of $PdCl_2$ (where Pd is in the +2 oxidation state) with cellobiose. In contrast to Pd, it is observed that $PdCl_2$ facilitates chain cleavage and ring rearrangements of the cellobiose unit. Subsequent investigations on individual ring structures further reveal a metal-promoted intramolecular reaction pathway toward levoglucosan formation. Levoglucosan (1,6-anhydro-D-glucopyranose (see Figure 3b)) is a very common product of carbohydrate pyrolysis. For this reason levoglucosan is used as a tracer[32] for cellulose in biomass pyrolysis and its production is related to the reaction conditions. As shown in Figure 3b, its chemical composition is essentially that of a single glucose unit *minus* a water molecule, producing a bicyclic-ring structure, where the $-CH_2O-$ group bonds intramolecularly to the anomeric carbon (C-1) of the initial glucose unit. Note the three −OH groups of the C2−C4 are in trans-axial orientation with respect to each other and the initial glucose ring has assumed a boat configuration. A detailed mechanism for the formation of levoglucosan from one of these fragments is presented in the following discussion.

From our previous studies using Pd atom on cellobiose, we observed that the most thermodynamically stable product was obtained when Pd inserted between the C-1 and the β-1,4-O1 of the chain. Hence, we place the linear $PdCl_2$ molecule in its

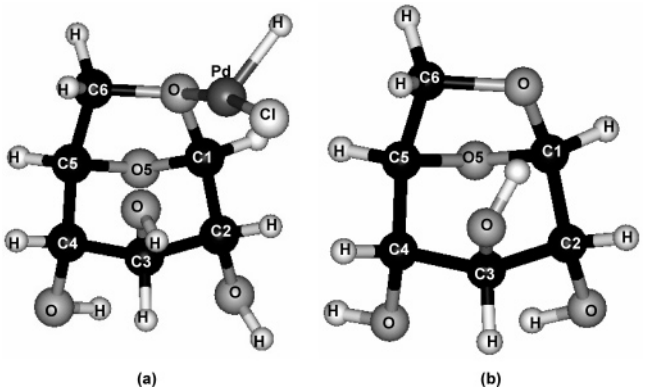

Figure 3. (a) The levoglucosan−Pd(H)Cl product complex. (b) A pure levoglucosan molecule. Table 3 compares their structural parameters.

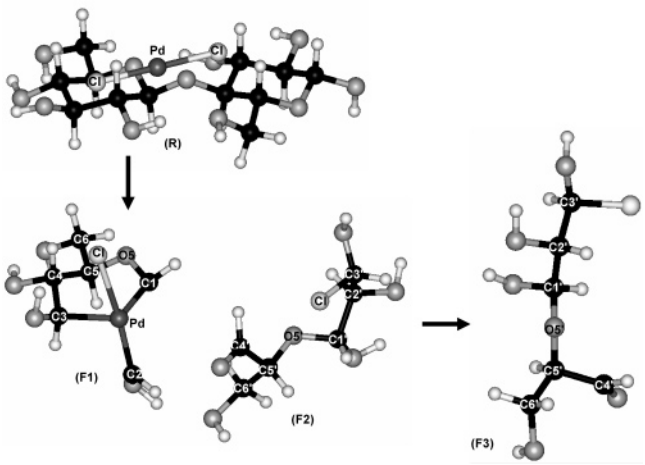

Figure 4. Fragmentation patterns as obtained from the interaction of $PdCl_2$ with cellobiose.

triplet ground state ($^3\Sigma_g^-$) with its Cl−Pd−Cl intermolecular axis parallel to the direction of the β 1−4 linkage bond axis of cellobiose as shown in (R) in Figure 4. This reacting system undergoes a fragmentation reaction forming two fragments (F1 and F2). F2 forms an aliphatic open chain chloro-compound with one of the Cl atoms from the salt incorporated in it (Cl attached to C3′). The other fragment F2 has the Pd bonded to three carbon atoms and one Cl atom as shown in F1 in Figure 4. We terminated the dynamics after the fragments were separated from each other beyond any reasonable bonding distance (the closest distance being 1.90 Å, between the H atom of the (C2−O−H) in F1 and the O atom of the (C6′−OH) in F2 in Figure 4; the rest of the distances are clearly beyond bonding interactions). It is to be noted that the fragments themselves remained intact in structure as shown in Figure 4, as they kept moving away from each other on further structural relaxation. This signified that these fragments are thermodynamically stable and will not undergo further fragmentations or other subsidiary reactions under the conditions imposed by our calculations. At this point we took F1 and F2 separately for closer analysis. It is to be noted that other conformations of approach of the $PdCl_2$ toward the cellobiose moiety, namely, the Cl−Pd−Cl molecular axis perpendicular as well as oblique to the direction of the polymer chain (polymerization) approaching the C1−β-1,4-O1 bond and Cl−Pd−Cl directly approaching the β-1,4-linkage O1 did not result in any kind of notable fragmentation products or otherwise.

After separation of the fragments, as described above, the aliphatic chloro-compound (F2 in Figure 4) did not cyclize back or undergo any further fragmentation reactions. The initial β-1,4-

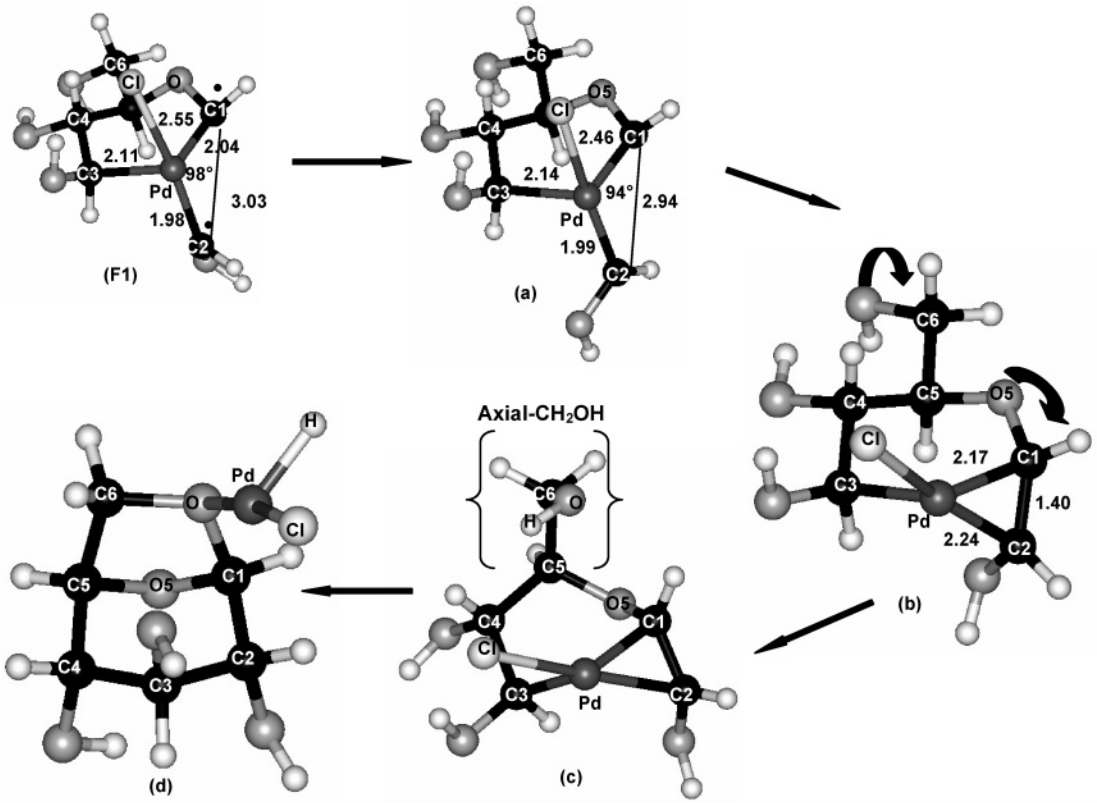

Figure 5. A tentative pathway to levoglucosan formation. (All bond lengths are in Å.)

O1, which remained in this fragment, formed an aldehydic functional group (F3 in Figure 4). One can speculate that under vigorous reaction conditions as in pyrolysis, several smaller aldehydes, alcohols, hydroxyaldehydes, and several other small organic molecules can be further formed from such fragments.

On the contrary, the fragment F1 containing the PdCl unit undergoes interesting intramolecular reactions to form a levoglucosan product complex. The initiation begins with a rotation along the Pd−C2 bond as shown in Figure 5, thus bringing the C2 and C-1 carbons closer to each other. The (C-1)−C2 distance changes from 3.03 Å to 2.94 Å and the C2−Pd−(C-1) angle changes from 98° to 94°. This species can be viewed as sort of a diradical (triplet state) with the unpaired electrons (denoted as •) on C-1 and C2 as shown in structure a of Figure 5 resulting in the lowering of energy by ∼0.27 eV (∼6.23 kcal mol^{-1}). This is followed by a single bond formation between C-1 and C2 as shown in structure b of Figure 5. This process is highly exothermic with enthalpy of reaction calculated to be ca. −3.46 eV (ca. −79.79 kcal mol^{-1}). The bond length between C-1 and C2 is calculated to be 1.40 Å. The Pd is still held by C-1, C2, and C3 in a η^3-type linkage with the Pd−(C-1), Pd−C2, and Pd−C3 bond lengths being 2.17, 2.24, and 2.07 Å, respectively. The Pd−Cl bond length is 2.41 Å. The next reactive intermediate that we identified is species c in Figure 5. Here the O5 puckers down and the $-CH_2OH$ group puckers up to an axial position. The rest of the atoms, namely C-1 through C5 and O5, form more or less a boat-like structure with no bond between the C2−C3 atoms. It is indeed interesting to note that in this species, a bulky $-CH_2OH$ group is in an axial position with the other two axial hydrogen atoms, as well as the Pd−Cl unit. From simple arguments of torsional interactions this structure would be expected to have a higher energy with respect to the precursor species, but energetics show otherwise. The frequencies obtained show that this is indeed a thermodynamically stable structure, which is a reactive intermediate and not

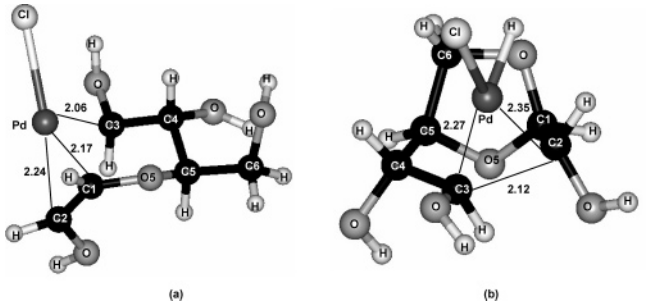

Figure 6. (a) Transition state of process 5b → 5c (see Figure 5). (b) Transition state of process 5c → 5d (see Figure 5).

a transition state species. The enthalpy change for this process is predicted to be ca. −0.16 eV (ca. −3.69 kcal mol^{-1}). The transition state structure for this molecular rearrangement is shown in Figure 6a. The transition state appears to be more like the reactant species shown in Figure 5b, where the −OH group assumes an axial position after undergoing a rotation about the C5−C6 bond. The activation energy for this process is calculated to be ∼0.27 eV (∼6.23 kcal mol^{-1}). From this intermediate species, the next step is predicted to be a concerted reaction process, whereby the Pd atom "grabs" the H atom from the $-CH_2O-H$ moiety and forms the H−Pd−Cl unit, which comes out of the Pd-η^3 linkage, leaving behind the resulting levoglucosan unit as shown in structure d of Figure 5. The enthalpy of reaction for this step is calculated to be ca. −0.07 eV (ca. −1.61 kcal mol^{-1}). The transition state structure for this molecular rearrangement is shown in Figure 6b. The activation energy for this process is calculated to be ∼2.34 eV (∼53.96 kcal mol^{-1}). In this activated complex structure one notes that the bond between C2 and C3 is forming (separated by 2.12 Å) and the PdCl unit is detaching from the η^3-type of Pd−C linkages while the Pd has already grabbed the H from the O atom of the $-CH_2O$ group. All the steps outlined in this

TABLE 2: Dissociation Pathways for the Levoglucosan−Pd(H)Cl Product Complex and Its Fragments

reaction dissociation	energy (eV)
(1) levoglucosan−Pd(H)Cl → levoglucosan−PdCl + H	2.65
(2) levoglucosan−Pd(H)Cl → levoglucosan−PdH + Cl	3.31
(3) levoglucosan−Pd(H)Cl → levoglucosan−Pd + H + Cl	5.84
(4) levoglucosan−Pd(H)Cl → levoglucosan−Pd + HCl	1.34
(5) levoglucosan−Pd(H)Cl → levoglucosan + Pd + H + Cl	6.30
(6) levoglucosan−Pd(H)Cl → levoglucosan + PdH + Cl	3.79
(7) levoglucosan−Pd(H)Cl → levoglucosan + PdCl + H	3.64
(8) levoglucosan−Pd(H)Cl → levoglucosan + Pd + HCl	1.81
(9) levoglucosan−Pd(H)Cl → levoglucosan + Pd(H)Cl	1.21
(10) levoglucosan−Pd → levoglucosan + Pd	0.47
(11) levoglucosan−PdH → levoglucosan + Pd + H	3.00
(12) levoglucosan−PdH → levoglucosan−Pd + H	2.53
(13) levoglucosan−PdH → levoglucosan + PdH	0.48
(14) levoglucosan−PdCl → levoglucosan + Pd + Cl	3.66
(15) levoglucosan−PdCl → levoglucosan−Pd + Cl	3.19
(16) levoglucosan−PdCl → levoglucosan + PdCl	1.00
other relevant side reactions:	
(17) Pd(H)Cl → Pd + H + Cl	5.10
(18) Pd(H)Cl → PdCl + H	2.44
(19) Pd(H)Cl → PdH + Cl	2.58
(20) Pd(H)Cl → Pd + HCl	0.60
(21) PdH → Pd + H	2.51
(22) PdCl → Pd + Cl	2.66
(23) 2Cl → Cl_2 ($\Delta E = -1.996$ eV)	
(24) 2H → H_2 ($\Delta E = -4.74$ eV)	

mechanism are entropically costly, especially the last step where the entropy decreases by ∼6 cal/(mol K) as the CH_2O- group gets locked into forming another ring on bonding to C-1. The formation of this second ring in turn takes away some degrees of freedom from the resulting molecular structure, which is not compensated by the formation of the H−Pd−Cl unit. So the reaction is an enthalpy driven process resulting from the bond formation as the H is "grabbed" by the Pd of the PdCl unit. The resulting H−Pd−Cl unit is bound to the levoglucosan molecule with a moderately strained Pd−O bond distance of 2.22 Å. The product complex levoglucosan−Pd(H)Cl is formed by a Pd←O "dative" bond. This situation of bonding is facilitated due to the diffused nature of the Pd valence orbitals. The already diffused 4d orbitals of Pd mix with the 5s−5p orbitals to some degree, while bonding occurs.[33] Thus, vacancies in the valence level of a Pd in a complex can accommodate charge from a donor atom like oxygen of the $-CH_2O-$ linkage in levoglucosan. Moreover, this highly diffuse valence shell of Pd makes it a more "polarizable" atom, which in turn contributes to its "H-grabbing" ability as seen in the final step of the levoglucosan formation. The various possible endothermic dissociation pathways of this HPdCl−levoglucosan unit under vigorous reaction conditions as in pyrolysis and their respective energetics are given in Table 2. To compare the structural parameters of levoglucosan in the product complex, we also calculated a stable structure for a levoglucosan unit as shown in Figure 3b. On comparison, we find that the bond parameters are essentially identical with variations beyond the first decimal place. Furthermore, to rule out a "stepwise" mechanism as opposed to a "concerted" mechanism of levoglucosan formation from intermediate c as outlined in Figure 5, we performed several calculations with a view to isolating reactive intermediates. In these structures, either there is a bond between C2−C3 (i.e., the boat is completely formed), the $-CH_2O(H)-$(C-1) bond is formed but the C2−C3 remains nonbonded, or a levoglucosan is formed with the PdCl unit still not close enough such that the Pd can "grab" the H from the $-CH_2O-H$ moiety. All these calculations resulted in structures which are either the precursor

TABLE 3: Structural Parameters of the Levoglucosan−Pd(H)Cl Product Complex and a Pure Levoglucosan Molecule[a]

	levoglucosan−Pd(H)Cl	levoglucosan
C1−C2	1.54	1.54
C2−C3	1.55	1.55
C3−C4	1.55	1.55
C4−C5	1.54	1.54
C5−C6	1.53	1.53
C5−O5	1.44	1.44
C6−O(C1)	1.46	1.44
O5−C1	1.40	1.41
C1−H	1.09	1.09
C2−H	1.10	1.09
C2−O(H)	1.43	1.41
C3−H	1.09	1.09
C3−O(H)	1.44	1.42
C4−H	1.09	1.10
C4−O(H)	1.42	1.43
C5−H	1.09	1.09
C6−H	1.09	1.09
C1−O5−C5	103	102
O1−C5−C6	100	100
C5−C6−O(Pd)	102	103
C6−O(Pd)−C1	107	107
(Pd)O−C1−O5	107	106
O−C1−C2	110	110
C6−C5−C4	116	114
O−Pd	2.22	
Pd−H	1.50	
Pd−Cl	2.31	
H−Pd−Cl	86	
H−Pd−O	101	
Pd−O−C6	114	
Pd−O−C1	117	

[a] Bond lengths are in Å and angles in deg.

of structure d in Figure 5, i.e., structure c, or other higher energy conformers with the Pd migration from η^3 to a η^2 type linkage cleaving the (C-1)−C2 bond and forming the C2−C3 bond as shown in Figure 7a. This unit is ∼0.9 eV (∼20.75 kcal mol^{-1}) higher in energy than the levoglucosan−Pd(H)Cl product in structure d of Figure 5. Similarly another higher energy structure that was obtained is shown in Figure 7b, which is ∼0.4 eV (∼9.22 kcal mol^{-1}) higher in energy than the levoglucosan−Pd(H)Cl unit. As is apparent from the energies of these two structures, it could be noted that none of them are logical reactive intermediates for the levoglucosan formation. Thus one can safely conclude that the Pd "grabbing" the H atom from the $-CH_2O-H$ moiety with the concerted formation of bonds between C2 and C3 and the O atom of the $-CH_2O$ and the anomeric carbon (C-1) forming the levoglucosan product complex is the most plausible mechanism under operation here. Moreover, the exothermicity of the Pd−H bond formation is the driving force for this reaction, even though it is not favored entropically. Thus, in this case Pd(II) also acts as an oxidation mediator of sorts. It is also worth mentioning here that another stable product was obtained in the above investigations (Figure 7c), where the PdCl unit is bonded to the O of the axial $-CH_2$-OH unit. This structure is ∼0.3 eV (∼6.92 kcal mol^{-1}) lower in energy than the levoglucosan−Pd(H)Cl unit in Figure 5d.

From our calculations we believe that the presence of $PdCl_2$ catalyzes the formation of levoglucosan from cellulose. Considering the structures of the reactive intermediates outlined in Figure 5, one finds that Pd acts as an "anchoring" agent to hold the otherwise unstable fragment (comprised of the open chain carbohydrate moiety) such that the intramolecular reactions can occur effectively, ending up in the final levoglucosan−Pd(H)-Cl product complex. In our other studies with $CuCl_2$ as well as

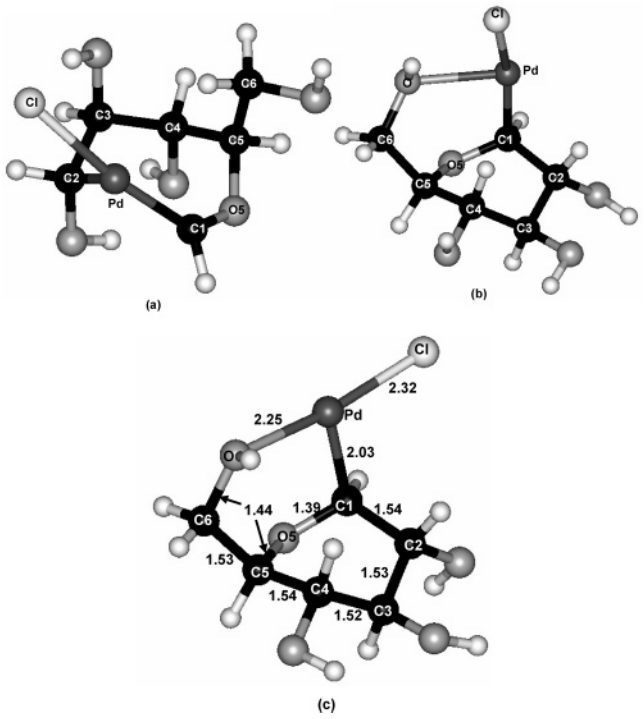

Figure 7. (a, b) High energy structures as obtained from the calculations, and thus ruled out as intermediates involved in the reaction described in Figure 3. (c) Another probable product of this reaction as described above. (All bond lengths are in Å.)

$CaCl_2$ we do not find any such "anchoring" by the metal atom and what remains instead is a pure organic fragment with the metal atom-containing inorganic moiety moved away. It is worth mentioning here that larger quantities of levoglucosan formation are observed only in the case of pyrolysis of cellulose in the presence of Pd (+2) salts, thus reinforcing our explanation that the "anchoring" effect of Pd facilitates levoglucosan formation, which is absent in the case of Cu and Ca where no metal C bonds are formed. Moreover, the H "grabbing" ability of Pd is also an important factor in the formation of the levoglucosan−Pd(H)Cl product complex.

IV. Conclusions

The reactions between Pd and $PdCl_2$ with cellobiose have been investigated by using density functional calculations. Pd is found to insert into a C−O bond site in the cyclic carbohydrate moiety with binding energies of ∼0.2 and ∼0.5 eV (∼4.61 and 11.53 kcal mol^{-1}) at the C1′−O5′ and the O1−(C-1) bonds, respectively. On the contrary, Pd(II) chloride is shown to promote the polymeric chain cleavage and ring rearrangements. The fragmentation pattern obtained from the interaction has also been discussed. One of these fragments is found to contain the Pd atom while the other is observed to be a pure aliphatic chloro compound. The fragment containing the PdCl unit is shown to undergo several stepwise intramolecular reactions to end up as a levoglucosan unit attached to a Pd(H)-Cl moiety. The overall reaction is exothermic and the reaction enthalpy was calculated to be ca. −3.69 eV (ca. −85.09 kcal mol^{-1}). In line with our investigations, it will be interesting to study the effect of other inorganic reagents on cellobiose and bring to light the differences and similarities in their fragmentation patterns as well as end products formation.

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