Cycloaddition of Carbonyl Compounds on Si(100): New Mechanisms and Approaches to Selectivity for Surface Cycloaddition Reactions

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Abstract: Density functional theory has been used to explore cycloaddition reactions of organic molecules containing carbonyl functional groups on the Si(100) surface. As with other π bonds, carbonyl groups can add to the surface by a [2+2] cycloaddition with negligible activation barrier, as previously shown through experiment. However, the present calculations indicate that 1,2-dicarbonyls, such as glyoxal, may also react by means of a [4+2] addition to form a hetero-Diels−Alder product in which the organic ring stands normal to the surface. Calculations of [2+2] and [4+2] pathways indicate that both reactions proceed without significant barriers. This reactivity is analogous to that of conjugated dienes, in which evidence for both reactions has been observed. In contrast to unsaturated alkyl systems, which must react through the π electron system, the reactions of carbonyls may proceed through a very different mechanism, in which the initial surface interaction is through the oxygen lone pair. The presence of lone pairs affects the geometry of the [4+2] adduct, and may alter the competition between [2+2] and [4+2] addition. Some potential rearrangement reactions of the initial binding products are described. Recent experimental studies of a 1,2-dicarbonyl on Si(100) are reinterpreted in light of these calculations, and found to be consistent with the presence of the [4+2] adduct. Finally, some molecules are suggested as cycloaddition reagents for experimental tests of the conclusions presented here.

I. Introduction

Interest in the chemisorption of organic molecules on semiconductor surfaces has been fueled by a variety of present and potential applications. The controlled deposition of organic films on surfaces has found applications in sensor technology, high throughput combinatoric analysis, optoelectronic devices, nonlinear optical materials, and microelectronics. By developing new reactions that might be used to form well-defined layers on silicon or other semiconductor surfaces, it is hoped that new methods may be developed that take advantage of the particular properties of these surfaces. In particular, the electronic response, ready availability of well-ordered single-crystal surfaces, inherent orientational order of the surface atoms, and the highly developed technology for accurate surface patterning provide unique opportunities for developing new devices on silicon.

These ideas have motivated a large number of recent theoretical and experimental investigations on the attachment chemistry of organic molecules on the Si(100)−(2×1) surface. Theoretical and experimental investigations have found that organic molecules with π bonds can react with the Si(100) surface dimer bond by a variety of cycloaddition mechanisms, in which the surface dimer reacts in partial analogy to a molecular double bond.[1−9] For molecules with a single unsaturated C−C bond, such as ethylene, the initial product of adsorption on Si(100) is the [2+2] cycloaddition product.[1−3] The surface [2+2] addition can be formally described as a rearrangement of two π electrons from a C=C bond, and two dangling-bond electrons from a surface dimer rearrange to form two Si−C σ bonds, resulting in a four-membered-ring cycloadduct (Scheme 1, X = CH_2). Analogous reactions through a N−N π bond are believed to account for the reactive adsorption of azo-*tert*-butane.[4]

For conjugated dienes, an alternative [4+2] cycloaddition reaction is possible.[5−9] This reaction was first predicted to occur using density functional theory,[5,6] and subsequently observed experimentally.[7−9] It is the surface analogue of the Diels−Alder reaction, which is widely used in organic synthesis. The [4+2] reaction formally involves the rearrangement of four π electrons of the diene and the two dangling-bond electrons of the dimer to form two Si−C σ bonds, resulting in a six-membered-ring cycloadduct (Scheme 2, X = CH_2 for addition of 1,3-butadiene).

However, dienes can also undergo the [2+2] reaction (Scheme 1, R = $CHCH_2$ for addition of 1,3-butadiene), and possible competition from this side reaction has been a concern since the earliest work on this subject.[5−9] While the [4+2] product is thermodynamically favored over the [2+2] product (primarily because the [4+2] product has less ring strain), there is at most a small barrier to either reaction, so that they may compete kinetically. In fact, the [2+2] addition product has been observed as a minority product in one experimental study of diene addition.[9] Such competition may limit the value of [4+2]

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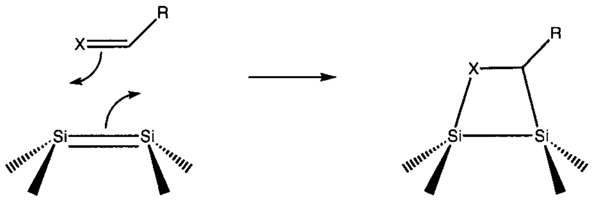
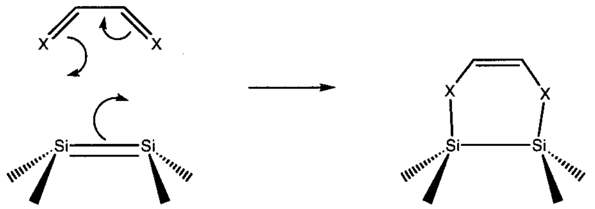
Scheme 1



Scheme 2



cycloaddition reactions in applications where a high degree of order is required.

One possible approach to controlling the competition between cycloaddition reactions can be found in the analogous reactions of disilenes, molecules with a Si−Si double bond.[10−13] Disilenes can only be isolated if they have bulky substituents (most commonly *tert*-butyl or mesityl) and some details of their chemistry depend on the particular group used. For example, not all disilenes react with 1,3-dienes, but when they do, it is by [2+2] addition.[10,11] On the other hand, heterodienes, such as benzil[12] (Ph(C=O)−(C=O)Ph) and 1,4-diazabutadienes[13] (RN=CH−CH=NR), react with disilenes to produce only the [4+2] product, even when those disilenes are entirely unreactive toward dienes. Hetero-Diels−Alder addition is observed even when the heterodienes themselves have bulky substituents (e.g., phenyl or *tert*-butyl), implying that [4+2] addition of dienes to disilenes is not simply prohibited by steric crowding of the disilene. The fact that heterodienes form exclusively the [4+2] product demonstrates that the kinetic barrier to [4+2] addition is substantially lower for heterodienes than for dienes, and that the relative barriers to [4+2] and [2+2] addition of heterodienes are reversed compared to those of hydrocarbon dienes.

Heterodienes have lone pairs available for reaction as well as π systems, and it is possible that the differing disilene cycloaddition chemistry of dienes and heterodienes reflects fundamental differences in mechanism. If this is the case, then the same mechanistic difference may operate in Si(100) surface chemistry. In this paper, we use first-principles theory to explore the cycloaddition chemistry of a series of carbonyl compounds (shown in Figure 1) on the Si(100)−2 × 1 surface. Just as for unsaturated C−C bonds, a single carbonyl bond may undergo [2+2] cycloaddition to the surface dimer, while a 1,2-dicarbonyl can react by either [2+2] or [4+2] cycloadditions (X = O in Schemes 1 and 2). However, we shall demonstrate that carbonyls can initiate reaction through the oxygen lone-pair electrons, instead of the molecular π system. Since the mechanism of reaction for carbonyl compounds can be so different from that for C=C double bonds, the kinetic competition between [2+2] and [4+2] reactions is likely be different for dicarbonyls than for dienes. It is not feasible to make reliable theoretical predictions of the branching ratio for two reactions with small or negligible activation barriers, but we hope that this work will motivate new experimental studies of the hetero-Diels−Alder reaction as a route to surface modification. Carbonyls were chosen as a prototype, because there have already been experimental studies on these compounds.[14,15] However, we expect that analogous compounds with C=N double bonds will react in a similar way, giving our results more generality.

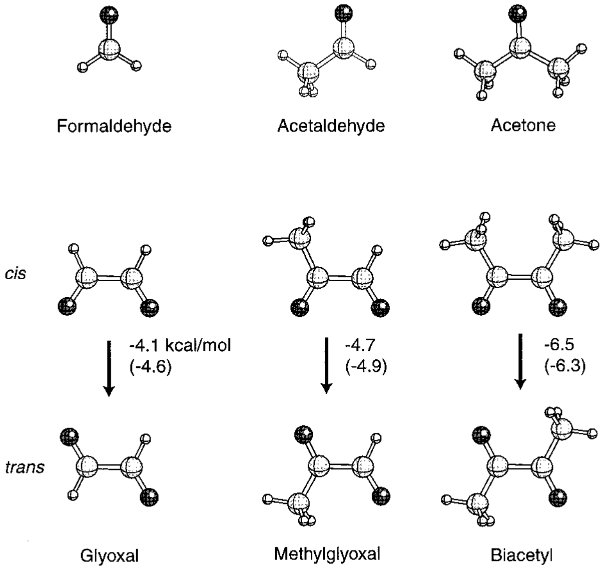


Figure 1. Carbonyl molecules studied in this paper. Differences in energy (kcal/mol, including zero-point energy) calculated for cis and trans conformations are shown for dicarbonyls (B3LYP/6-31G(d), followed by B3LYP/6-311++G(2df,2p) in parentheses).

Note that we do not address the adsorption of carbon monoxide in this study. While CO also has a carbon−oxygen π bond, it cannot react by cycloaddition through that bond, because the product would be carbene-like (with a lone pair on a carbon having roughly sp^2 hybridization). Such species are not expected to be stable and are not observed in adsorption of CO on Si(100).[16,17] By itself, the fact that [2+2] cycloaddition products are not observed might simply indicate that there is a kinetic barrier to their formation. However, prior theoretical work confirms that the cycloaddition product is substantially higher in energy than desorbed CO,[18] as expected for a carbene.

In the next section we describe the theoretical methods used in this work. We discuss the structure and thermodynamics of the chemisorption products in Section III.A, and the reaction paths to formation of prototypical [2+2] and [4+2] products in Section III.B. Adsorbates containing oxygen often rearrange after adsorption, and some possible rearrangements for carbonyls and dicarbonyls are described in Section III.C. Comparisons are made to existing experimental data in Section III.D, and a reinterpretation of some of that data is proposed. New experimental studies are proposed in Section III.E to test some aspects the theoretical picture developed here, and concluding remarks are made in Section IV.

II. Models and Methods

The calculations in this work were carried out using the B3LYP hybrid Density Functional Theory (DFT) method[19,20] as implemented

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in Gaussian 98.[21] This method has been successfully used to predict binding energies and reaction barriers in good agreement with experiment for a number of reactions on Si(100), including other cycloaddition reactions.[5,6] Predictions of the B3LYP method[5,6] for cycloaddition reactions on Si(100) have also been reproduced with reliable wave function methods (CASSCF with second-order perturbative corrections).[22] B3LYP has also been shown to be accurate in predicting activation energies for molecular cycloadditions.[23−27]

In the present calculations, a 6-31G(d) basis was used for geometry optimizations. The full Hessian matrix was calculated for each optimized structure to confirm that a true minimum had been reached. The frequencies from this calculation have been scaled by 0.95 for zero-point energy (ZPE) corrections and comparison to measured vibrational frequencies. All reported binding energies include the ZPE. A larger 6-311++G(2df,2p) basis was used to calculate single-point energies of optimized geometries to test the basis set sensitivity of the reaction energies. Reaction pathways were investigated with both the 6-31G(d) and an intermediate 6-311+G(d) basis; energies along the reaction paths do not include the ZPE.

The Si(100)−2 × 1 surface is modeled by a Si_9H_{12} single dimer cluster. No geometry constraints on either atomic positions or overall symmetry were applied in reaction path studies. However, some constraints were used in all reported calculations of minimum energy structures. Using the geometry of a Si_9H_{12} cluster (with unpassivated surface dangling bonds) optimized with C_{2v} symmetry as a template, all atoms of the fourth and third layers and the hydrogens of the second layer are fixed in their positions. No constraints are applied to the silicon atoms of the dimer or second layer. These constraints have little effect on the initial adsorption products, but for rearrangement products where atoms may be inserted into Si−Si bonds, constraints are essential to retain structures consistent with the possibilities on an extended surface.

III. Results and Discussion

A. Structure and Energetics of Chemisorption Products. We have considered the cycloaddition products of all the species shown in Figure 1. For the simple aldehydes and ketones, only a [2+2] addition product is possible, while for the dicarbonyls either a [2+2] or [4+2] addition product is possible. Structures and energies (relative to the lowest energy conformations of the separated reactants) of the cycloaddition products are shown in Figure 2.

In all cases, the [2+2] cycloaddition product is energetically favored over reactants, with binding energies ranging from 38 to 51 kcal/mol. Increased substitution at the carbon bound to the surface consistently reduces the magnitude of the binding energy. The [2+2] products are stabilized by formation of strong Si−C and Si−O bonds in exchange for breaking weaker Si−Si and C−O π bonds. However, some of this strength is compromised by strains inherent in the four-membered ring. Indications of strain are evident in the surface adduct geometries; typical values of geometric parameters are shown in Figure 2. Si−O, Si−C, and C−O bond lengths are slightly longer than average bond lengths found in the Cambridge structural database.[28] The Si−Si dimer bond is slightly shorter than that calculated on the monohydride surface. Furthermore, the C−Si−Si and O−Si−Si bond angles average 71° and 82°, respectively, far smaller than the ideal tetrahedral value of 109.5° expected for 4-fold coordinated, sp^3 silicon. In fact, the bonding hybridization of the surface silicons serves asan indicator of ring strain. Using Natural Bond Orbital (NBO) analysis,[29] the orbitals contributed by the Si atoms to the Si−Si bond are described as sp^n hybrids, with n ranging from 3.5 to 5.0 (values of n are included as labels along Si−Si bonds for some typical cases in Figure 2). The increased p-character along this bond reflects the strain resulting from the four-member-ring geometry. Finally, we note that methylglyoxal has two inequivalent carbonyls and that an alternative [2+2] addition product is possible. This alternative product is energetically less stable than the product shown in Figure 2 (with a binding energy of only 45 kcal/mol); its properties can be understood by analogy with the other species described here, and will not be described in any further detail.

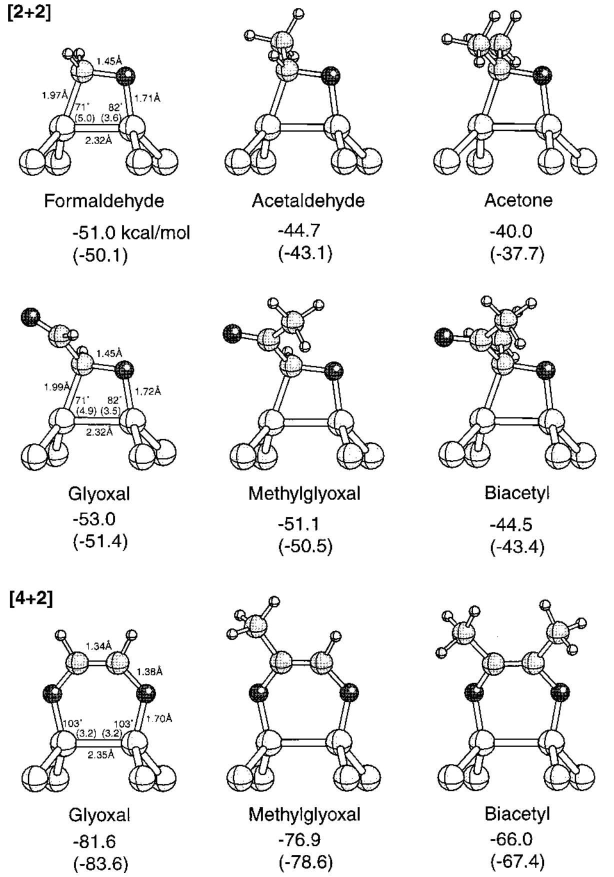

Figure 2. Products of cycloaddition reactions between the molecules of Figure 1 and the Si(100) surface. Energies (kcal/mol, including zero-point energy) relative to reactants are listed under each structure (B3LYP/6-31GZ(d), followed by B3LYP/6-311++G(2df,2p) in parentheses). Adsorbate bond angles with respect to the dimer bond, selected bond lengths, and the sp^n hybrid contributed by each Si atom to the dimer bond are shown for formaldehyde and glyoxal products.

The [4+2] cycloaddition product of a dicarbonyl, also known as the hetero-Diels−Alder product, has two Si−O bonds. These products are substantially more stable than the corresponding [2+2] products, with binding energies ranging from 67 to 84 kcal/mol (Figure 2). The stronger binding energy of the [4+2] product reflects the greater strength of Si−O bonds (compared to Si−C bonds) and the reduced strain in a six-member ring.

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Again, substitution at carbon is associated with weaker binding. Bond lengths in the [4+2] complexes are slightly longer than the average database values for molecular species,[28] with deviations similar to those in the [2+2] complexes. However, the dimer bond length is slightly longer than that in the [2+2] complexes. More importantly, the bond angles on surface silicons are closer to tetrahedral values (103° O−Si−Si angles for surface-bound glyoxal) allowing sp^n hybrids with $n = 3.2$ for both surface Si atoms.

Some novel aspects of the hetero-Diels−Alder products can be seen by comparing the analogous cycloaddition products of glyoxal and butadiene.[6] The orientation of the rings in the [4+2] products are qualitatively different, with the glyoxal adduct lying in a plane normal to the surface, while the butadiene adduct lies in a plane tilted away from the surface normal (by about 40°).[6,8] As a result, the glyoxal adduct will not cause as much steric crowding of the adjacent dimer site as dienes. This structural difference is a consequence of the differences in hybridization of the atoms bound to silicon. The carbon of butadiene is sp^3 hybridized (it is bound to four other atoms) and has a tetrahedral geometry. In contrast, the oxygen from glyoxal can accommodate its lone pairs in sp^2 or sp^3 hybrids; the planar sp^2 geometry is favored because it allows more extended delocalization of the π and lone-pair electrons. Another important difference between glyoxal and butadiene is the greater binding energy for the addition products of glyoxal. The [4+2] and [2+2] binding energies are 82 and 53 kcal/mol for glyoxal, but only 68 and 42 kcal/mol for butadiene[6] (all calculated at the B3LYP/6-31G(d) level). This is again a consequence of the greater strength of Si−O bonds over Si−C bonds.

B. Reaction Pathways. Using glyoxal as a prototype, we have explored reaction paths for both [2+2] and [4+2] additions. We find that there are paths for each reaction with no significant activation barrier. Attempts to locate transition states were unsuccessful. Instead, each reaction path was followed by an energy minimization initiated from a geometry composed of reactant structures at a large intermolecular distance.

To probe the [2+2] pathway, the trans isomer of glyoxal was positioned above the silicon dimer with a Si−O distance of 3.2 Å and the Si−C distances of 4.1 Å (Figure 3a), approximately 1.5 and 2.4 Å longer, respectively, than the distances in the adsorbed product. From this initial geometry, in which the energy was only 0.85 kcal/mol greater than the energy of the isolated reactants (including counterpoise correction; ZPE is not included, but should be negligible at this initial geometry), the optimization proceeded directly downhill to the [2+2] product. The initial step is the highest energy point on this path, and no local minima were encountered in the optimization.

Two different pathways were explored for the [4+2] addition, both involving the cis isomer of glyoxal. No reaction barrier was found in either case. In the first case, cis glyoxal was aligned so that one carbonyl bond is coplanar with the dimer bond (Figure 3b). This initial geometry is nearly identical to that used in the study of the [2+2] reaction path, the only exception being that glyoxal is in the cis conformation, rather than trans. The initial geometry had a Si−O distance of 3.2 Å and an energy of −0.6 kcal/mol (counterpoise corrected, without ZPE) relative to the isolated reactants. An optimization was allowed to proceed without constraint. Although the glyoxal placement was intentionally chosen to favor formation of the [2+2] product, remarkably, energy minimization caused the molecule to reorient and follow a direct path downhill to the [4+2] product. Thus, there is apparently a barrier to [2+2] addition from the cis conformation, but no barrier for [4+2] addition. In the second [4+2] addition path, glyoxal was positioned above the dimer bond with both Si−O distances measuring 3.2 Å (Figure 3c). The molecule is tilted away from the surface normal, and positioned so that the π orbitals on oxygen can overlap with the surface dangling bonds, similar to the path followed by dienes.[5,6,22] Beginning with a geometry that is 1.2 kcal/mol above the isolated reactants (counterpoise corrected, without ZPE), the optimization proceeded directly downhill to products (Figure 3c). No symmetry or other constraints were imposed on the system. Again, the initial step was the highest energy point and there was no evidence of any local minima other than the cycloaddition product.

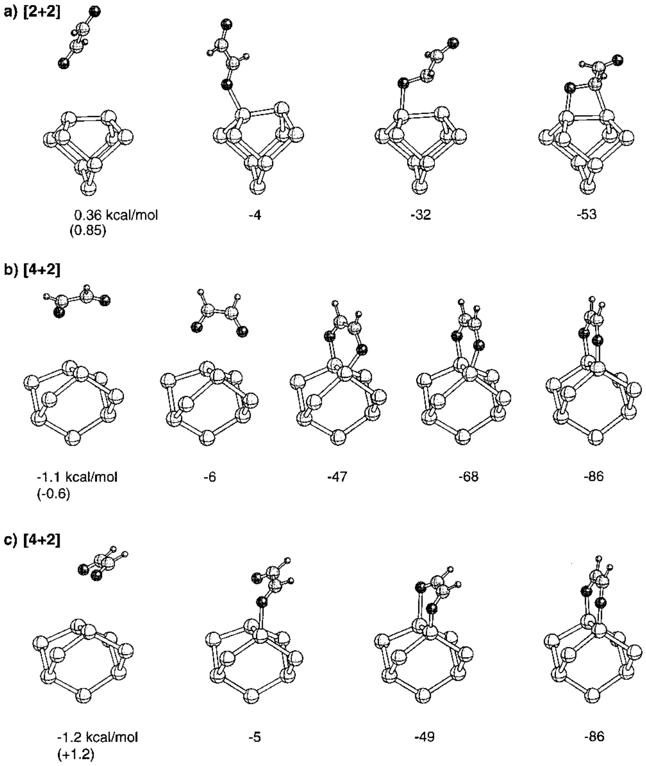

Figure 3. A series of geometries on the reaction path for cycloadditions of glyoxal: (a) [2+2] additionand (b and c) [4+2] addition paths. Energies (B3LYP/6-31G(d)) are given in kcal/mol relative to the isolated reactants (without any zero-point energy correction). Counterpoise-corrected energies for the initial geometry are given in parentheses.

Note that the [4+2] pathway has been explored for the cis isomer of glyoxal. Our calculations indicate that cis isomers of dicarbonyls are higher in energy than trans by 4−6 kcal/mol (Figure 1). Thus, while [4+2] addition is thermodynamically favored, it must compete kinetically with [2+2] cycloaddition. Since the [2+2] reaction from the trans conformation appears to be unactivated, the small equilibrium population of the cis conformation appears to disfavor the [4+2] addition. However, the kinetic competition also depends on entropic considerations. This latter issue is difficult to address with first-principles theory, as it requires sampling an ensemble of paths by molecular dynamics or Monte Carlo methods. We have investigated only a few possible paths to [4+2] adsorption. It is even possible, for example, that a barrierless pathway exists for [4+2] addition from molecules initially in the trans conformation. Ultimately, the branching ratio between the two paths will have to be determined experimentally. However, it is noteworthy that [2+2] addition appears to be kinetically unfavored in the cis conforma-

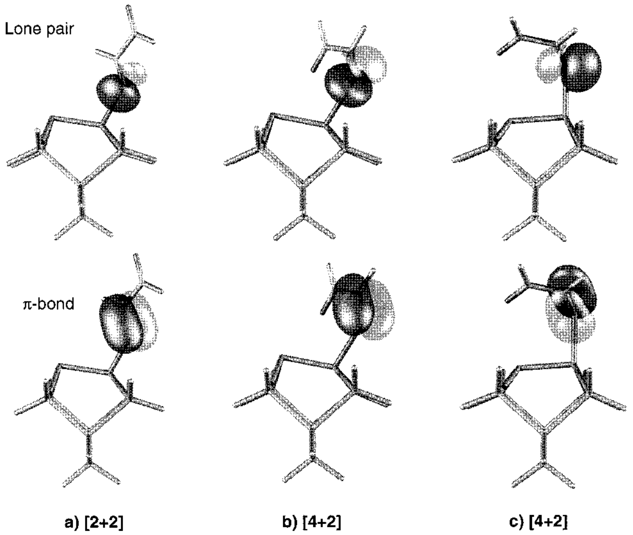

Figure 4. Natural bond orbitals for the oxygen lone pair and π orbital nearest to the surface for the three mechanisms shown in Figure 3. In each case, the geometry is the same as the second step shown in Figure 3 for the corresponding reaction path.

tion. This suggests that molecules in which the cis conformation is enforced will react more selectively to form the [4+2] product.

Analysis of the orbitals along these reaction paths shows that carbonyls and dicarbonyls can react by mechanisms that are fundamentally different from those for alkenes and dienes. While [2+2] and [4+2] cycloadditions of unsaturated hydrocarbons involve only the π electrons, carbonyl compounds have the possibility of interacting through either the π electrons or the oxygen lone pairs. Figure 4 shows Natural Bond Orbitals[29] corresponding to the π bond and the lone pair nearest the surface, in geometries taken from early stages in the reaction paths (on each path, it is the second geometry shown in Figure 3a−c). For both the [2+2] path (Figures 3a and 4a) and the first of the [4+2] paths (Figures 3b and 4b), the oxygen lone pair is directed along the Si−O axis, allowing a strong overlap with the surface dangling bond. On the other hand, the Si−O axis is in the nodal plane of the π orbital, so that there will be little net overlap of the surface dangling bond with the π orbital. Thus, both of these reactions can be mediated by the lone pair electrons, providing new pathways that are not present for alkenes or dienes. Note that pathways involving the π orbitals remain available. Figure 3c shows a path for the [4+2] reaction that is similar to the path for butadiene. The molecule is oriented so that the π orbitals can overlap with the surface dangling bonds while the orientation of the lone pairs does not allow strong overlap with the surface orbitals. Nevertheless, the lone pair mechanism can be expected to change the selectivity of these reactions, altering the competition between [4+2] and [2+2] addition.

Such a difference in selectivity has a known precedent in the analogous molecular reactions of disilenes, as discussed in the Introduction. While 1,3-dienes react with disilenes to form the [2+2] product exclusively,[10,11] reactions with heterodienes produce only the [4+2] product.[10−13] Dicarbonyls, diazabutadienes, and acylimines (conjugated C═O and C═N double bonds) can all react through either the π system or the nitrogen lone pairs, and all are known to form the hetero-Diels−Alder product with disilenes. The analogy with our calculations for glyoxal suggests that the dramatic difference between the reactivity of disilenes with dienes and heterodienes reflects the difference between mechanisms mediated by π electrons and those mediated by lone pairs. Furthermore, this chemical precedent implies that the difference in mechanism will lead to a similarly strong preference for the [4+2] product in surface reactions of heterodienes.

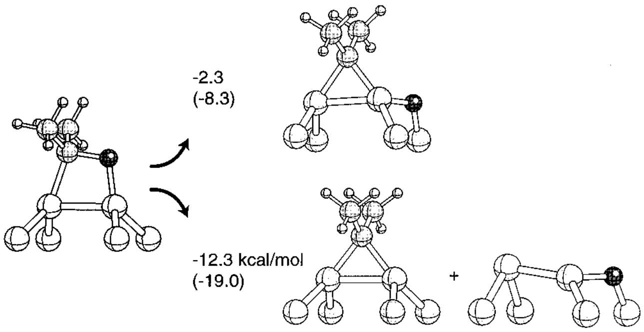

Figure 5. Some possible rearrangements of the [2+2] acetone cycloadduct. Energies (kcal/mol, including zero-point energy) shown are relative to the initial cycloadduct (B3LYP/6-31G(d), followed by B3LYP/6-311++G(2df,2p) in parentheses).

C. Rearrangement Products. Although both [2+2] and [4+2] additions of carbonyls produce strongly chemisorbed cycloadducts, it is possible for both of them to rearrange to lower energy isomers. Theoretical and experimental investigations have found that oxygens in surface-bound species almost inevitably migrate so as to insert into Si−Si bonds, though this may require elevated temperatures.[14,15,30,31] We have investigated the energetics of several candidate rearrangements resulting from oxygen migration from both [2+2] and [4+2] cycloadducts. Some additional possibilities have been discussed in the context of nitromethane rearrangements.[32]

Some rearrangements of the [2+2] acetone product are shown in Figure 5. The structures shown result from oxygen migration into the back-bond immediately adjacent to the surface adduct, or into a neighboring dimer. Both oxygen migrations leave the remaining portion of the surface cycloadduct to form a surface-bound alkane, attached via a Si−C−Si three-membered ring. Both oxygen migrations are energetically allowed, though neither has a strong driving force; oxygen migration to another dimer is slightly preferred over back-bond insertion. We have observed similar trends for the surface rearrangement of surface-bound nitromethane.[32] More detailed analysis in that case showed that the relative stability of different rearrangement structures depends on the strengths of the bonds formed, ring strain in the cycloadduct, and the associated strains created within the lattice.

We have also compared the energetics for the rearrangements of the [2+2] and [4+2] glyoxal cycloadducts (Figure 6). There are more possibilities than for acetone, since two oxygen atoms can migrate. However, the [4+2] product is more stable than the [2+2] product, so rearrangements from the [4+2] product are always less favorable. Structures **I** and **II** are analogous to the acetone rearrangement products, and are again thermodynamically favored with respect to the initial [2+2] addition product. However, these structures are disfavored with respect to the [4+2] cycloadduct. Structures **III** and **IV** are more strongly favored, since they have less ring strain and one more Si−O bond than **I** and **II**. There is a substantial driving force to reach **III** or **IV** from either the [2+2] or [4+2] adduct. In all cases, oxygen migration to another dimer is favored over back-bond insertion. Structures in which both oxygens have inserted

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[30] Weldon, M. K.; Stefanov, B. B.; Raghavachari, K.; Chabal, Y. J. *Phys Rev. Lett.* **1997**, *79*, 2851.

[31] Stefanov, B. B.; Gurevich, A. B.; Weldon, M. K.; Raghavachari, K.; Chabal, Y. J. *Phys. Rev Lett.* **1998**, *81*, 3908.

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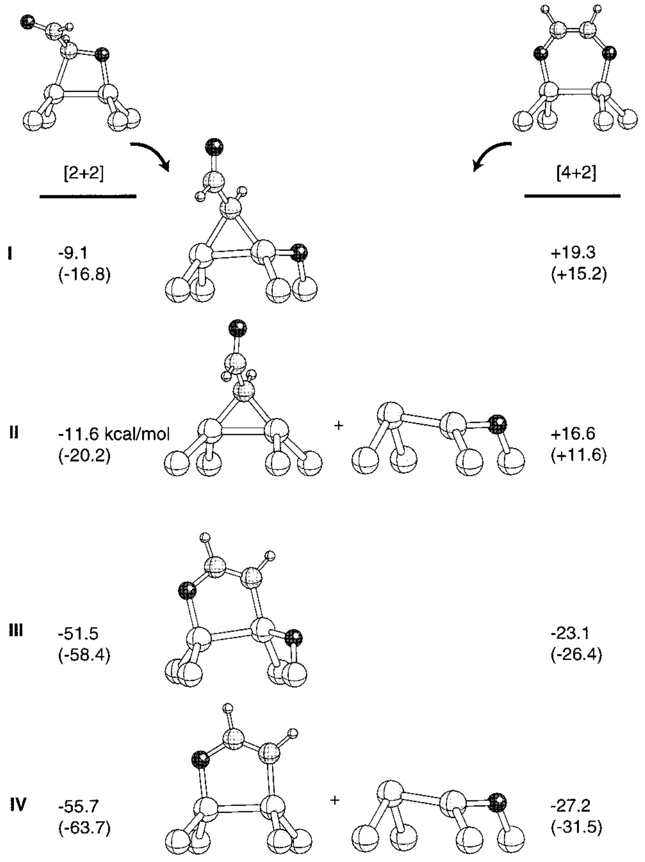


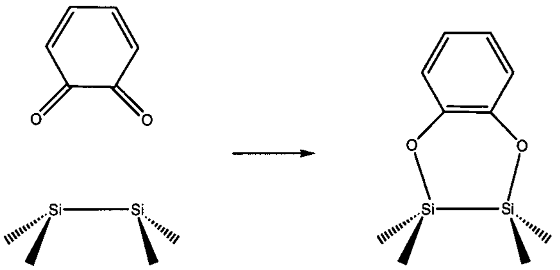
Figure 6. Some possible rearrangements of [2+2] and [4+2] glyoxal cycloadducts. Energies shown (kcal/mol, including zero-point energy) are relative to the initial cycloadduct (B3LYP/6-31G(d), followed by B3LYP/6-311++G(2df,2p) in parentheses).

into Si−Si bonds are also possible. While we have not calculated the energies of any such structures in this case, simple considerations of bond strengths imply that they will be even more stable than the structures shown.

We have not explored the kinetic barriers to rearrangement. Some oxygen rearrangements, such as those occurring after adsorption of water, occur only at elevated temperature.[30,31] In the case of nitromethane adsorption, it appears that rearrangements to form Si−O bonds occur spontaneously at room temperature. However, the driving force for rearrangement of nitromethane[32] is much greater than that for carbonyls. As described in the next section, there is experimental evidence that the adsorption products of carbonyls and dicarbonyls do rearrange at relatively low temperatures.

D. Comparison with Experiment. Experimental studies by Armstrong et al. have shown that acetone, acetaldehyde, and biacetyl irreversibly chemisorb to the Si(100) surface.[14,15] The high sticking probability is consistent with barrierless adsorption. Among their results, Armstrong et al. showed that roughening the surface with sputtering greatly reduced the chemisorption of these molecules, consistent with the interpretation that the dimer bond is required for chemisorption. For acetone and acetaldehyde, X-ray photoelectron spectra (XPS) indicate that bonds to both C and O are formed, and high-resolution electron energy loss spectra (HREELS) indicate the absence of a carbonyl peak.[14] These results were interpreted as evidence that these carbonyl compounds adsorb on the surface via [2+2] cycloaddition. However, the XPS spectra also show evidence of other products in which the C−O bond is completely cleaved, comparable to those in Figure 5. These peaks appear even at low temperature. This is consistent with the interpretation that rearrangements from an initial [2+2] adsorption product occur with little activation barrier, though we cannot rule out the possibility that an entirely different dissociative chemisorption reaction (as yet unspecified) competes with [2+2] addition to create multiple surface species.

Scheme 3



Experimental studies of biacetyl adsorption are more ambiguous. Armstrong et al. suggested that biacetyl adsorbs to form a [2+2] product, in analogy to acetone and acetaldehyde.[15] Just as for the (mono)carbonyls, several species are evident in the XPS at low temperature. However, while one would expect a substantial carbonyl adsorption for the [2+2] adduct of biacetyl, the only evidence in HREELS is a weak peak at 1670 cm^{-1} (our calculations predict that this carbonyl stretch would be at 1696 cm^{-1}). Armstrong et al. assigned this peak to the free carbonyl of the [2+2] adduct, attributing its weak intensity to the orientation of the carbonyl. We propose an alternative interpretation of these observations: if biacetyl primarily adsorbs to form the thermodynamically favored [4+2] product, no carbonyl peak would be expected. In this case, the weak peak observed at 1670 cm^{-1} would be assigned to the alkene C=C stretch in the [4+2] product (which we predict to be at 1675 cm^{-1}). The mixture of adsorption products observed would be understood as the result of rearrangement reactions after adsorption. The existing experimental data do not distinguish unambiguously between the two possible cycloaddition products. Nevertheless, the [4+2] product appears to be consistent with the data, and should be considered in the experimental interpretation.

E. Controlling Kinetics and Thermodynamics: Test Cases. On the basis of our calculations and the review of available experimental data, we can suggest some new experimental tests of the factors that control selectivity of cycloadditions on Si(100). While precedents from disilene chemistry imply that heterodienes favor the [4+2] path over the [2+2] path, it is not clear whether the reaction of biacetyl on Si(100) follows the same trend. In fact, biacetyl is a bad example if one hopes to favor [4+2] addition, since it has the largest cis−trans isomerization energy of the examples we have studied. On the other hand, our calculations imply that enforcing a cis geometry will favor [4+2] addition by raising an activation barrier to [2+2] addition. This suggests several possibilities.

o-Benzoquinone is a dicarbonyl in which the ring structure enforces a cis conformation. Several reactions are possible for this molecule. The product with the strongest thermodynamic driving force is the [4+2] cycloadduct of the carbonyls (Scheme 3). Because this reaction forms an aromatic ring, the reaction energy is −109 kcal/mol relative to reactants. This is overwhelmingly more favorable than the carbonyl [2+2] cycloadduct (−54 kcal/mol relative to reactants). However, benzoquinone may also undergo [2+2] or [4+2] addition via the unsaturated C−C bonds. The [4+2] addition product should have a binding energy similar to cyclohexadiene (−54 kcal/mol), which in turn is essentially the same as the carbonyl [2+2] adduct of benzoquinone. The least favored product will be the [2+2] adduct to a C═C bond. If thermodynamics determines the product distribution, only the hetero-[4+2] product will be seen. However, [4+2] addition to the 1,3-diene should have a negligible barrier and thus may compete kinetically (though it may be possible to favor reaction through the carbonyls by attaching bulky substituents to the ring). Our calculations on dicarbonyls and those of others[22,33] on dienes indicate that there are barriers to the [2+2] additions from the cis conformation that would keep them from competing kinetically. It would be valuable to test these predictions experimentally.

Competition between the [4+2] and [2+2] additions of a *cis*-dicarbonyl can be explored directly with 1,2-cyclohexane dione (the analogue of *o*-benzoquinone with a saturated ring). Though the hetero-[4+2] product of this molecule will not obtain aromatic stabilization upon adsorption, there is no concern about side reactions through the ring. Thus, this molecule offers a direct test of our prediction that the cis conformation should favor the [4+2] cycloaddition.

Finally, for all of these molecules there is the possibility of rearrangement after the initial product is formed. This issue can be avoided by using the analogous 1,4-diazabutadienes, in which the oxygens of the dicarbonyl are replaced with nitrogen. The diazabutadienes can again react through a lone pair, but there is no thermodynamic driving force for migration of nitrogen into back-bonds (Si−N bonds are much weaker than Si−O bonds). As noted above, diazabutadienes show the same preference for [4+2] addition as diketones in reactions with disilenes.[13] Thus, the reactivity we have described for diketones should have analogues in nitrogen heterodienes that are less likely to rearrange at low temperature.

IV. Conclusions

First-principles calculations show that carbonyl compounds undergo cycloaddition reactions with the Si(100)−2 × 1 surface with little or no activation barrier. Carbonyl compounds may react to form a [2+2] product, with a four-membered ring. Experimental evidence for such structures has been obtained by Armstrong et al.[14] Molecules containing two adjacent carbonyl bonds may also undergo [2+2] reactions, though a [4+2] hetero-Diels−Alder reaction is thermodynamically favored. The ring in the [4+2] product stands normal to the surface, so that there is minimal crowding of adjacent dimers. We have suggested a reinterpretation of experiments[15] on adsorption of biacetyl that is consistent with the [4+2] cycloadduct as the major product. Both the [2+2] and [4+2] complexes can rearrange to lower energy structures by oxygen migration to adjacent dimers or back-bonds. We have not considered chemisorption paths that involve addition across adjacent dimers, though this is another possibility that may produce multiple surface products, and it deserves further consideration in interpreting experiments on heterodiene adsorption. We also note that there are some subtle electronic and surface strain effects that are neglected in the single dimer model, and these may alter binding energies or adsorption energies by a few kilocalories per mole.[34,35]

The reactions of carbonyls demonstrate a new mechanism for reaction on Si(100) surfaces. In contrast to the reactions of unsaturated hydrocarbons that proceed through the π electrons, carbonyls can initiate reaction through interactions with the oxygen lone pairs. This means that different factors will affect the selectivity of the cycloadditions for dienes and dicarbonyls. Similar reactions are expected for other heterodienes, such as diazabutadienes, where rearrangements after adsorption are not a concern. Thus, the class of hetero-Diels−Alder reactions offers new opportunities for controlled functionalization of Si(100).

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