C₅H₅ on a Pt(111) Surface: Electronic Structure and Bonding

Graciela Brizuela and Roald Hoffmann*
Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301
Received: May 20, 1998; In Final Form: August 26, 1998

The chemisorption of cyclopentadienyl (c-C₅H₅) on Pt(111) has been studied using qualitative band-structure calculations in the framework of the tight-binding implementation of the extended Hückel method. We modeled the metal surface by a two-dimensional slab of finite thickness, with an overlayer of c-C₅H₅ per nine surface Pt atoms. The c-C₅H₅ molecule is attached to the surface with its five C atoms bonding mainly with three Pt atoms. The Pt−Pt bonds in the underlying surface and the C−C bonds of c-C₅H₅ are weakened upon chemisorption. Forward-donation from the adsorbate to the substrate is significant, and there is also substantial back-donation, as reported in the literature for benzene on Pt and Ni surfaces. We found that the band of Pt 5d,2 orbitals plays an important role in the bonding between c-C₅H₅ and the surface, as do the Pt 6s and 6p,3 bands.

1. Introduction

The study of molecules adsorbed on metal surfaces is important from both a practical and a theoretical point of view. There is a vast petrochemical industry based on the catalytic conversion of aliphatic linear-chain hydrocarbons to aromatic and branched species. It is widely accepted that isomerization and dehydrocyclization of C₅ paraffins occur via cyclic C₅ adsorbed intermediates. A number of studies have examined the structure and chemistry of this class of molecules on Pt₄−¹⁰ and other transition metal surfaces. N. R. Avery has reported vibrational electron energy loss spectroscopy (EELS), work function changes (WFC), and thermal desorption spectroscopy (TDS) observations for cyclopentane, cyclopentene, and cyclopentadiene adsorbed on Pt(111). These cyclic molecules are easily dehydrogenated as the temperature of the substrate increases. During this heating process, cyclopentadienyl (c-C₅H₅) is produced at 250 K; this species is stable to temperatures near that required for long chain alkane (C₅) skeletal isomerization (T ≈ 500 K). Later work of C. T. Campbell et al., based on bismuth postdosing TDS, supports Avery’s proposals. Moreover, c-C₅H₅ has been identified as a stable intermediate on Cu(100) and Rh(111), arising from the dehydrogenation of either cyclopentene or cyclopentadiene.

While there are several experimental studies devoted to the chemisorption of cyclic hydrocarbons on transition metals, theoretical studies are relatively scarce and mainly focused on the adsorption of C₆ species and especially benzene. Recently, C. Minot et al. analyzed the preferred adsorption site and geometry of benzene on Pt(111) using the extended Hückel method (EHT). P. Sautet et al. reported calculations for benzene on Pt(111) and Rh(111) using the same method; the results were in substantive agreement with experimental results.

The objective of the present work is to study the chemisorption of c-C₅H₅ on Pt(111) at low coverages. The model is considered in the next section.

2. Adsorption Model and the Computational Method

Our calculations were performed using the extended Hückel method, an approximate molecular orbital scheme, implemented with the YAEHMOP package. This method is not reliable for energetic and geometry optimization, but captures well the essential orbital interactions in chemisorption. Geometrical optimization of a cluster model for c-C₅H₅ on Pt(111) had been carried out previously using the atom superposition and electron delocalization (ASED) molecular orbital method. In the present study we modeled the system by a two-dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the metallic surface. A three-layer slab was employed as a compromise between computational economy and reasonable accuracy. The molecule was adsorbed on one side of the slab.

The adsorption geometry needs to be discussed in some detail. N. R. Avery proposed a possible geometrical model for c-C₅H₅ on Pt(111): taking into account the van der Waals dimensions of c-C₅H₅, the maximum coverage of 2.1 × 10¹⁴ molecules cm⁻² can be achieved with a (√7 × √7) R19° surface net, which could be compared with the TDS estimate of 1.5 × 10¹⁴ molecules cm⁻². Avery also suggested that the C₅ rings might rotate relative to each other in order to minimize repulsive interactions, and that it is sterically possible for them to adopt orientations which would allow the coadsorption of atomic hydrogen, released after the dehydrogenation of the precursor (c-C₅H₅). F. C. Henn et al. studied the adsorption of c-C₅H₅ with X-ray photoelectron spectroscopy (XPS), found that approximately four Pt atoms were required to accommodate one molecule. According to XPS results, the maximum absolute coverage of c-C₅H₅ that could be produced from a single heating of adsorbed c-C₅H₅ was 0.140 ± 0.012. This value is in agreement with the one proposed earlier by N. R. Avery for saturation coverage of c-C₅H₅ on Pt(111).

Even though there is no low energy electron diffraction (LEED) determination of the surface structure, considering the
coverage values estimated by N. R. Avery and F. C. Henn et al. and our previous theoretical work, we decided to adopt a P(3 × 3) surface structure. This is shown in Figure 1. Our calculations indicate that for this coverage there is no adsorbate—adsorbate repulsion. According to ref 4 the experimental energetic description of such interactions are beyond the simple MO methods we use. The molecule was assumed to lie parallel to the surface, as suggested in the literature. In a previous work we have considered several adsorption sites on Pt(111): 1-fold, 2-fold, and 3-fold octahedral and 3-fold tetrahedral. The C5 ring was also rotated in each position and the C—C, C—H, and C5—Pt distance optimized. For the tricoordinated sites, the adsorption energies were similar. In keeping with the results of our optimization study, c-C5H5 was placed in the most favored coordination site (3-fold tetrahedral). We used the previously optimized geometry: interatomic C—C and C—H distances of 1.55 and 1.15 Å, respectively (even though we realize these are somewhat too long), a molecule center to surface separation (C5—Pt) of 2.00 Å, and bending of ring hydrogens 27° away from the surface. Pt—Pt bond lengths were kept fixed at the bulk value of 2.77 Å. No surface reconstruction or relaxation was included.

The density of states (DOS) of both c-C5H5 and Pt and the crystal orbital overlap population (COOP) curves between atoms and orbitals were calculated in order to analyze the adsorbate—surface interactions. The COOP curve is an energy-resolved plot of the overlap population-weighted density of states. Integration of the COOP curve up to the Fermi level gives the total overlap population (OP).27

### 3. Isolated Cyclopentadienyl System

We know from organometallic chemistry that interactions between metal atoms and bonded ligands occur mainly through the frontier orbitals of both components. These orbitals for planar c-C5H5− are, in order of increasing energy, 3e′′ (a degenerate σ orbital set, doubly occupied), 1a1′′ (π orbital), 1e″ (degenerate π orbital set, highest occupied), and 1e′′′ (degenerate π orbital set, unoccupied). Normally, the σ orbitals of the molecule are not though to enter into bonding with an external ligand; nevertheless, we include the 3e′′ set because it will turn out that it does play a role in surface bonding.

When the molecule is chemisorbed, the hydrogens bend away from the surface. There is some s, p mixing, but overall, the effect is small. Accordingly, we will proceed by labeling the c-C5H5− orbitals in D3h symmetry. The frontier orbitals mentioned above are sketched in Figure 2.

In analyzing the bonding of cyclopentadienyl in a discrete molecule (e.g., a metallocene, Cp2Fe, or CpMLn, in general) or on a surface (the problem at hand) a question arises: should we think of the ligand (adsorbate) as neutral (c-C5H5) or as an anionic (c-C5H5−)? The molecule of course does not care; it binds or chemisorbs, making whatever electron shifts it needs to maximize bonding. The problem is ours, and it affects the explanations we construct: if we begin with c-C5H5− (the e′′′ HOMO completely filled) then there will invariably be much net electron transfer to the metal. On the other hand, if we start with neutral c-C5H5, the 1e′′′ occupied by only 3 electrons, we will get less forward-donation. This is not reality, just the arbitrary choice made by us of a starting description of the fragments.

Fully aware of this ambiguity, in this paper we choose the c-C5H5− starting point, simply because it gives us a closed shell description for the cyclopentadienyl fragment.

### 4. The Chemisorption System

In Figure 3 an interaction diagram is shown, similar to those used in molecular chemistry. At left is the DOS of a two-dimensional monolayer of c-C5H5−, arranged in the same geometry as the molecules take on the surface. All the molecular orbitals are at the same energy that they have in the isolated species. The 1e′′′ and 1e′′ bands correspond to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of one molecule, respectively. Judging from the narrowness of these bands, there is no adsorbate–adsorbate interaction revealed by the extended Hückel method. Nevertheless, it is reasonable to think that the coverage is fixed by very weak adsorbate–adsorbate interactions. None would be expected, since the shortest H−H contact between neighboring molecules in the model is 3.74 Å.

At right in Figure 3 is the DOS of the bare neutral Pt(111) surface slab model. The position of the Fermi level shows that most of the d band is filled. The computed electronic configurations of the surface and bulk (three-dimensional) Pt atoms are indicated in Table 1. The occupation of the valence s orbitals seems to be slightly lower and that of the p orbitals substantially greater than that would have been anticipated. This is a consequence of the low energy of the 6p basis orbital in our parameter set. The surface-layer of the slab is negatively...
charged relative to the bulk; a consequence of the greater number of interactions (contacts) experienced by a bulklike atom. The width of the d band is approximately 8.0 eV for the bare Pt-(111) surface and 8.4 eV for the bulk (three-dimensional) Pt, thus the bulk atom states are more spread out. These values are in agreement with ab initio and semiempirical results reported in the literature \(W_d = 7.9\, \text{eV}\)\(^{32,33}\). The dispersion of the s and p bands is much larger than that of the d band, indicating the much more contracted nature of the d orbitals.

The DOS of the chemisorbed system c-C\(_5\)H\(_5^-\) on Pt(111) is displayed in the middle of Figure 3. The shaded area shows the contribution of the states of the chemisorbed molecule. The Fermi energy of the metal surface moves slightly (0.16 eV), because of the finite thickness of the slab and electron transfer between slab and adsorbate.

More information is obtained when we look at what happens to each molecular orbital of c-C\(_5\)H\(_5^-\) upon adsorption. The contributions to the DOS of each of the c-C\(_5\)H\(_5^-\) frontier orbitals, magnified by a factor of 5, are shown in Figure 4. The horizontal sticks display the energy of the molecular orbitals in magnified by a factor of 5, are shown in Figure 4. The horizontal sticks display the energy of the molecular orbitals in the isolated, planar species. It is apparent that the HOMO \(1\epsilon'_0\)" and LUMO \(1\epsilon''_0\) are very dispersed, indicative of strong interaction with the metal surface. After adsorption, the whole \(1\epsilon''_0\) band is spread over ca. 12 eV, and 35% of its DOS is pushed up above the Fermi level. The \(1\epsilon''_0\) FMO (the lowest \(\sigma\) orbital of c-C\(_5\)H\(_5^-\)) also interacts significantly; 17% of the DOS is pushed up above of the Fermi level and the main body of this FMO is pushed down ca. 0.8 eV. Even the \(\sigma\) \(3\epsilon'_0\) band is substantially dispersed; the main body of the band is pushed down 0.4 eV. To use organometallic language, this means that significant forward-donation from c-C\(_5\)H\(_5^-\) to the surface has occurred. Meanwhile, the main body of the \(1\epsilon''_0\) band is pushed up ca. 1.2 eV and this fragment molecular orbital (FMO) becomes ca. 18% occupied. This interaction is the surface counterpart of metal to ligand back-donation. Obviously c-C\(_5\)H\(_5^-\) interacts very strongly with this surface.

The computed OPs between atoms are listed in Table 2. We see that the C–C OP is significantly decreased (\(\approx 15\%\)), indicative of a weakening of the C–C bonds. On the other hand, the C–H bonds are slightly strengthened (\(\approx 3\%\)). There also develops a large bonding OP between C and Pt atoms. The Pt–Pt OP decreases, and for the metal atoms nearer to the ring (Pt\(_1\), Pt\(_3\)) the OP returns to a value close to that calculated for the bulk. A way to think about this is as partial recovery of the lost coordination of the surface metal atoms upon adsorbing c-C\(_5\)H\(_5^-\). The strong adsorbate–surface bonding requires that both C–C and Pt–Pt intrinsic bonding decrease. This result was also found in the adsorption of benzene and unsaturated C\(_2\) hydrocarbons on Pt(111)\(^{23,31}\).

In Table 2 we include the OP of those bonds which contribute significantly to the c-C\(_5\)H\(_5^-\) adsorption. These are mainly C\(_1\)-Pt\(_1\), C\(_3\)-Pt\(_3\), and C\(_2\)-Pt\(_1\) (the numbering of the atoms is shown in Figure 5). These bonds contribute ca. 22 (\(\times 2\)), 26, and 11 \((\times 2)\) \%, respectively, of the overall bonding. Interestingly, although the C\(_2\)-Pt\(_3\) distance is shorter than the C\(_2\)-Pt\(_1\) distance, the OP of the former bond is approximately four times smaller than that of the latter. Thus, c-C\(_5\)H\(_5^-\) is adsorbed to the surface with its five carbons bonding mainly to three Pt atoms (Pt\(_1\), Pt\(_3\), and Pt\(_4\)). Arguing from the EELS spectra of c-C\(_5\)H\(_5\)/Pt-(111), Aver’ proposed that the cycle is covalently bound, with an attachment of five C atoms to the surface.\(^5\)

Let us examine the bonding between c-C\(_5\)H\(_5\) and the surface in closer detail by considering the COOP curves for C\(_1\)-Pt\(_1\), C\(_3\)-Pt\(_3\), C\(_3\)-Pt\(_1\), and C\(_2\)-Pt\(_1\) bonds displayed in Figure 6. The contributions to the right (left) of the vertical axis are bonding (antibonding) between the specified atoms. Among the filled levels, three important regions may be distinguished in Figure 6a. Regions I and II are formed by the sharp peak at \(-15\) eV and a broader region with a maximum value at ca. \(-13.4\) eV, respectively. Region III begins from the top of region II and goes up to the Fermi level; it contains a bonding peak at ca. \(-11.4\) eV.

Of the frontier orbitals, the \(1\epsilon''_0\) band is the major component of region I (10% of \(1\epsilon''_0\)"); however, the peak in this region is mainly due to the contribution of an inner \(\sigma\) orbital (87% of \(3\epsilon_0\)”). In region II can be found 81% of the DOS of \(3\epsilon''_0\) (the highest \(\sigma\) orbital set of c-C\(_5\)H\(_5^-\)), 66% of \(1\epsilon''_0\)”, 36% of \(1\epsilon''_0\)”, and 9% of \(1\epsilon''_0\)”. The main c-C\(_5\)H\(_5^-\) contributions to the DOS in region III are of \(3\epsilon''_0\), \(1\epsilon''_0\)”, and \(1\epsilon''_0\)” (19, 26, and 7% respectively). The bonding in region II can be described as ligand (adsorbate) \(3\epsilon''_0\), \(1\epsilon''_0\)”, and \(1\epsilon''_0\)” to metal forward-donation, as well as metal to \(1\epsilon''_0\)” back-donation. The bonding in region III is partly the result of \(3\epsilon''_0\) and \(1\epsilon''_0\)” to metal forward-
donation and partly that of metal to 1e'' back-donation. The participation of 3e'' and 3a' (σ orbitals) along with the π orbitals (1a'', 1e'', and 1e''') is analogous to the orbital mixing found for benzene on Pt(111). The net result of these several interactions is a broad region of Pt–C bonding with small regions of antibonding, presumably the result of Pt–C anti-bonding combinations not pushed above the Fermi level.

The bending of hydrogens out of the carbon plane in discrete molecular LxM(CH)ν complexes (ν = 3–8 and M a transition metal) is traced to π interactions and reorientation of the π orbitals for better overlap. This bending toward or away from M depends on the size of the ring and the electronic structure of the MLν fragment. For C4R5 coordinated to a single metal center in a molecular complex, there is actually little bending away of the ligands. When c-C5H5− is adsorbed on the Pt surface and the geometry optimized, the lowest energy is achieved with substantial bending of ring hydrogen atoms away from the surface. Obviously there is involvement of the σ system of the molecule in bonding to the surface; this shows up in the dispersion and depopulation of 3e'' (see Figure 4).

In Table 3 the calculated orbital electron occupations for the c-C5H5− FMOs and the net charge on the molecule are listed. It can be seen that the 1a'' and 1e'' orbitals undergo significant depopulation upon adsorption, while 1e''', initially empty, is partially occupied. The net charge is determined by these electron occupations and small changes in other FMOs; in toto a significant electron transfer (=1.6e−) from the c-C5H5− molecule toward the surface has occurred. The forward-back-donation from 1a'' and 1e'' is greater than the metal to 1e'' back-donation of electrons, so the adsorbed molecule emerges positively charged relative to c-C5H5−. It is important to recall at this point the arbitrary choice of a monoanionic c-C5H5− starting point in our calculations, which was guaranteed to create maximum donation to the surface. Similar charge transfer was reported for benzene on Pt(111) using ASED. Ab initio CI calculations (reported by Z. Jing and J. L. Whitten) show a slight increase in energy of the Fermi level and a decrease in the energy of the benzene 1s SCF levels, suggesting that the molecule transfers charge to their Ni cluster model for the surface.

To obtain further more information about the adsorbate–surface interactions, we studied the contribution to chemisorption of the individual atomic orbitals of the C and Pt atoms. The corresponding atomic orbital occupations are displayed in Table 4. It can be seen that after adsorption both Pt1 and Pt3 undergo significant depletion of d orbitals (by 0.507 and 0.578 e−, respectively) while the Pt1, Pt4 s, and Pt1 d orbitals depopulate to a lesser extent (0.120 and 0.092 e−, respectively). The Pt p and the C s, p, and d orbitals show only small changes (less than 0.05 e−).

The contribution of the Pt4 d2 orbital to the total DOS is shown in Figure 7. It may be seen in Figure 7(b) that the d2 band spreads out above the Fermi level after adsorption. For this last curve, the lower peak at −13.5 eV matches with the sharp peak of the 1a'' molecular orbital, while the −12.6 and −11.4 eV peaks find their counterpart in the 1e'' curve (see Figure 4). The peak at ca. −6.8 eV matches that of 1e'''.

<table>
<thead>
<tr>
<th>Bond</th>
<th>c-C5H5−/Pt(111)</th>
<th>c-C5H5−/monolayer</th>
<th>Pt</th>
<th>Pt</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C−C</td>
<td>0.812</td>
<td>0.953</td>
<td>0.785</td>
<td>0.773</td>
<td>0.354</td>
</tr>
<tr>
<td>C−H</td>
<td>0.294</td>
<td>0.398</td>
<td>0.322</td>
<td>0.398</td>
<td></td>
</tr>
<tr>
<td>Pt−Pt</td>
<td>0.440</td>
<td>0.516</td>
<td>0.516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1−Pt</td>
<td>0.224</td>
<td>0.082</td>
<td>0.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2−Pt</td>
<td>0.021</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3−Pt</td>
<td>0.021</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C4−Pt</td>
<td>0.021</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5−Pt</td>
<td>0.021</td>
<td>0.021</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fermi level, eV</td>
<td>−9.65</td>
<td>−10.67</td>
<td>−9.81</td>
<td>−9.32</td>
<td></td>
</tr>
</tbody>
</table>

* Averaged over several slightly nonequivalent C−C, C−H, and Pt−Pt bonds.
we have here is an interaction between the whole $d_{z^2}$ band of Pt and the $1a_2''$, $1e_1''$, and $1e_2''$ molecular orbitals of c-C$_5$H$_5^-$. Some of the Pt s states (not shown) move above the Fermi level after adsorption. These orbitals have the majority of their states at energies lower than −12 eV. The s band therefore interacts mostly with $1a_2''$ and $1e_1''$ molecular orbitals. Similar results are found for the Pt$_4$ orbitals.

The principal orbital by orbital contributions to the new C−Pt OP’s induced by chemisorption are shown in Table 5. For C$_1$−Pt$_4$ and C$_1$−Pt$_1$ it can be seen that the bond is mainly due to overlaps between the p$_z$ orbital of C and the s, p$_z$, and d$_{z^2}$ orbitals of the metal and that p$_y$ and d$_{x^2}$ orbitals contribute more than the s orbital. This is in agreement with the expectation that the p$_z$ orbitals of the carbon ring are important participants in the frontier molecular orbitals (see Figure 2). Also, it can be seen in Table 4 that the C$_2$ orbital is depopulated more than other orbitals. The lobes of these orbitals are well oriented to overlap with the metal s, and especially with p$_z$ and d$_{z^2}$ metal orbitals.

We can also analyze orbital by orbital contributions to the COOP curves. In Figure 8 these curves between the p$_z$ orbital of C$_3$ and the s, p$_z$, and d$_{z^2}$ orbitals of Pt$_4$ are displayed. It can be seen that the first and second curves are mostly bonding, even for energies above the Fermi level. The C$_3$ p$_z$−Pt$_4$ d$_{z^2}$ states begin to be antibonding close to the Fermi level; above it they are always antibonding. The analysis is consistent with previous considerations. For instance, referring back to the regions defined in Figure 6 and the accompanying discussion, Figure 8 supports the interpretation that the peak at ca. −15 eV in region I is due to the interaction between Pt s and C p$_z$ orbitals, while in regions II and III there are contributions to the bonding from Pt s, p$_z$, and d$_{z^2}$. Region III is antibonding close to the Fermi level; this is due to the C p$_z$ and Pt d$_{z^2}$ antibonding states. Similar results were found for C$_1$−Pt$_1$ bond.

We can see from Table 5 that for the C$_2$−Pt$_3$ bond the s, p$_z$, and d$_{z^2}$ orbitals on the metal are the strongest contributors to the overall adsorbate−surface bonding. In the case of C$_2$−Pt$_3$
bond the s and p₂ orbitals on the metal are important; however, this bond is relatively weak.

As the chemistry of most transition metals is dominated by their d orbitals, the role of the s and p orbitals in chemisorption is seldom discussed, although these orbitals should interact with the adsorbate in a way analogous to their role in organometallic compounds. There is no doubt that the d orbitals are involved in the bonding with the surface, but the contributions of the metal s and p bands are also important. On bonding to the surface, c-C₅H₅ and the Pt 6s and 6p₂ orbitals interact strongly with Pt 5d orbitals as well as Pt 6s and Pt 6p₂ orbitals. In a related study, ab initio calculations for benzene on Ni(111) have shown a significant interaction between benzene π orbitals and Ni 3d and 4s orbitals.¹⁷

5. Conclusions

In the present theoretical study we have analyzed the adsorption of c-C₅H₅ on Pt(111). This molecule is strongly chemisorbed. C₃H₅ is attached to the surface with its five C atoms bonding mainly to three Pt atoms. Forward-donation from the adsorbate to the substrate is also present, as reported in the literature for benzene on Pt and Ni surfaces. The Pt−Pt bonds of the surface and the C−C bonds of the adsorbed hydrocarbon are weakened after chemisorption. We find that Pt 5d₂ states play an important role in the bonding between c-C₅H₅ and the surface, as do the Pt 6s and 6p₂ orbitals (z being the direction normal to the surface). Other similarities with benzene on Pt(111) include relatively little back-donation and significant bending back of the hydrogens away from the surface, with attendant σ−π mixing.

Acknowledgment. G.B. thanks FOMEC-UNS for a fellowship which makes possible her stay at Cornell University. Our work was also supported by a NSF Grant CHE 94-08455. We are grateful to the Cornell Center for Materials Research for its support of this research through Grant DMR-9632275.

Appendix

The tight-binding extended Hückel method was employed to trace the orbital interactions. The parameters for C, H, and Pt were taken from a previous study, and are listed in Table 6.

The $H_{ii}$ for C have been decreased by 1.0 eV and those of Pt increased by the same amount in order to minimize exaggerated electron drifts. Double-$\zeta$ expansions of the metal d orbitals were employed. The off-diagonal Hamiltonian matrix elements were computed with the modified Wolfsberg–Helmholtz formula. An 18 k point set for average properties calculations was obtained according to the geometrical method of R. Ramirez and M. C. Böhmi. Additional tests were conducted with different parameters set. Although the parameter choice influences quantitatively the results, the qualitative aspects are maintained.

References and Notes
