Formation of monocarboxylic acids and polyols on a graphite surface

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Abstract

A heterocatalytic model involving the graphite surface, which has been previously used for the surface formation of chemisorbed amino acids, is consistently extended to the synthesis of monocarboxylic acids and polyhydroxylated compounds. Extensive computations with semi-empirical and ab initio quantum chemical methods have been carried out to analyze reaction pathways on surface models of different sizes. The model assumes surface recombinations involving small functional groups. Polymerization is initiated by either a carboxyl (COOH) or a formyl (HCO) group that is anchored to the graphite surface through two chemisorption sites, and proceeds by the addition of mobile diffusors of the type \(\text{CH}_n\text{(COOH)}\) and \(\text{CH}_n\text{OH}\) \((1 \leq n \leq 3)\) and \(\text{CH}_n\text{OH}\) \((0 \leq n' \leq 2)\). Polymer length is determined by the competition between surface diffusion and hydrogenation. Some of the features observed in the laboratory regarding the surface self-assembly of monocarboxylic chains, in the organic inventory of star-forming regions and in carbonaceous meteorites can be addressed with the present approach.

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1. Introduction

The catalytic capabilities of a model graphite surface in the synthesis of simple amino acids have been previously studied with quantum chemical methods [1]. It is found that chemisorbed species can be built up from adsorbate–adsorbate (a–a) and adsorbate–free (a–f) surface processes in a hydrogen-rich environment where the surface essentially acts as a template. We report here calculations that show that such mechanisms can be consistently extended to the surface formation of monocarboxylic acids and polyhydroxylated compounds (polyols) such as sugars, sugar alcohols and sugar acids.

The surface formation of organic molecules is of interest in astrochemistry due to the observation of simple organic acids and sugars in star-forming regions (hot molecular cores). Both acetic acid (\(\text{CH}_3\text{COOH}\)) [2] and glycolaldehyde (\(\text{CH}_2\text{OHCHO}\)) [3] have been detected in the Sgr B2 Large Molecule Heimat (LMH). An origin for these molecule in grain-surface chemistry has been suggested as a result of their association with other complex organic grain products, and it is speculated that the assembly of functional groups on the grain surface accounts for the high degree of isomerism displayed. The subsequent detection in the LMH of ethylene glycol (\(\text{HOCH}_2\text{CH}_2\text{OH}\)), the reduced alcohol of glycolaldehyde, hints again at a low-temperature chemistry on the grain surface or ice mantles [4], and the presence of aldehydes such as propynal (\(\text{HC}_2\text{CHO}\)), propenal (\(\text{CH}_2\text{CHCHO}\)) and propanal (\(\text{CH}_3\text{CH}_2\text{CHO}\)) [5] constitutes strong evidence for reaction pathways based on successive hydrogenations.

Carbonaceous chondritic meteorites, e.g. Murchison, Murray and Orgueil, have traditionally been rich sources of organic compounds such as sugars, sugar alcohols, sugar...
mono-acids and di-acids and deoxysugar acids [6]. Mono-
carboxylic acids have been quantified in both straight-
and branched-chain isomers in concentrations that
decrease with increasing number of carbon atoms, the
signature that supports extraterrestrial abiotic synthesis
[7]. Aliphatic carboxylic acids with straight and branched
chains of up to 12 and 9 carbon atoms, respectively, have
also been identified in carbonaceous chondrites found in
Antarctica in concentrations that decrease logarithmically
throughout [8].

Scanning tunnelling microscopy (STM) has been a pow-
erful technique for laboratory studies of the properties of
chemisorbed self-assembled monolayers which have tech-
nological applications in multiple fields [9]. In the case of
organic thin films, STM has been hampered by image rec-
ognition, but the two-dimensional ordering of straight-
chain hydrocarbons is being resolved. For instance, it has
been found that carboxylic esters physisorb as linear chains
on the surface of highly oriented pyrolytic graphite
(HOPG) with the plane of the carbon skeleton parallel to
the surface, a different geometry from that displayed in
the gas phase [10–12]. The HOPG surface has also been
used for the template-directed assembly of proteins, where
it is found that the threefold symmetry of the graphite tem-
plate is reproduced in the adsorbate assembly [13].

A current difficulty in molecular electronics is the mas-
tering of the molecule–electrode bond, particularly in the
case of metal electrodes. A promising alternative is to use
a single-walled carbon nanotube (SWNT) covalently at-
tached to an organic molecular bridge, e.g. amine end
groups connected to carboxylic acid chains [14]. Further-
more, the SWNT capacitance is sensitive to surface adsor-
bates, an effect that can be used for the construction of
high-performance sorption-based sensors by thinly coating
the SWNT with chemoselective material [15].

Motivated by such diverse interest in organic surface
chemistry, and following earlier work [1], we study the for-
mation of organic species on a model graphite surface
starting from simple functional groups. Since we are con-
cerned with fairly large molecular structures and an exten-
sive number of reaction routes, our computational strategy
involves the use of both ab initio and semi-empirical quan-
tum chemical methods. Apart from its effectiveness, this
approach also leads to useful validations and accuracy esti-
mates of the underlying physical chemistry. In Section 2 the
graphite surface models and the numerical methods are de-
scribed, followed by an analysis in Section 3 of the surface
chemistry of functional groups in a hydrogen-rich environ-
ment. The syntheses of monocarboxylic acid chains and
polymers are developed in Sections 4 and 5, and our findings
are discussed in Section 6.

2. Surface models and numerical methods

Active surfaces are assumed to be of finite and variable
size, an important problem being the dependency of reac-
tion pathways on surface model size. As shown in Fig. 1,
three graphite surface models are considered: PAH1, a
coronene molecule (C_{36}H_{12}); PAH2, circumcoronene
(C_{54}H_{18}); and PAH3, circumcircumcoronene (C_{96}H_{34}).
In the optimization of the adsorbate–substrate system, sub-
strate relaxation is taken into account, and the surface
chemisorption sites of interest are on top of a carbon atom,
to be referred hereafter as site A, and on the bridge between
two carbon atoms, site B [16,17]. Surface chemistry is as-
sumed to occur via Langmuir–Hinshelwood adsorbate–
adsorbate (a–a) and Eley–Rideal adsorbate–free (a–f)
recombinations. The graphite surface model has been chos-
en in the present work for its simplicity, general interest in
different fields and for the lack of reliable experimental
data on surface composition and configurations, particu-
larly in the astrophysical context.

The numerical strategy we have adopted is to use a rela-
tively fast semi-empirical method, namely cativic [18], to
map out reaction routes which are then validated at a high-
er computational cost with the ab initio Gaussian 98 package
[19]. Cativic is a second-generation, semi-empirical, quan-
tum chemical package based on parametric Hamiltonians
within the MINDO/3 scheme of separating atomic and dia-
tomic parameters [20], the parametric functional compo-
nents of the total energy being similar to those in the
MINDO/SR implementation [21]. It offers a powerful gra-
phic user interface for molecular building and for display-
ing geometrical optimization routes. Data obtained with
this method are referred to hereafter as CAT. Computa-
tions with Gaussian 98 are carried out in a density-func-
tional-theory mode (B3LYP) with the bases 3-21G
(hereafter GA1) and 6-31G** (hereafter GA2). In 3-21G
two-basis functions are used to represent each valence
atomic orbital while 6-31G** uses polarization basis sets.

Experimental data for formic and acetic acids are em-
ployed to benchmark these two numerical methods. For
formic acid, it may be seen in Table 1 that GA1 and
GA2 reproduce the experimental bond lengths and angles
to better than 5%. CAT can also account for bond lengths
to this accuracy, but differences as large as 11% are found
for some bond angles. The CAT heat of formation agrees
with experiment to better than 5%, perhaps due to the fact
that the functional parameters for small organic molecules
in cativic are optimized with this quantity. The GA1 value,
on the other hand, differs from experiment by 30% but is
improved to 12% in GA2 at a notably higher computa-
tional cost. A similar situation is found for acetic acid
(Table 2) where the measured bond lengths and angles are
reproduced by all three methods to better than 4% while
the GA1 heat of formation is again poor. In spite of the
higher accuracy of GA2, its computational cost makes it
impractical to study surface processes on the relatively
large surface models that are being considered in this work.
Therefore, cativic results will be hereafter validated with
GA1. These comparisons indicate that the accuracy of
computed energies is not entirely reliable. On the other
hand, a useful measure of bond strength is the Wiberg
index computed by CATIVIC which is a quantity close to the bond order.

3. Surface functional groups

We have studied the formation of organic molecules on graphite model surfaces via a–a and a–f recombinations that involve simple functional groups of the type HCO, COOH, COH, CHOH, CH₂OH, CH, CH₂ and CH₃. They can be generated as products of basic surface reactions starting from chemisorbed atomic C and O that get progressively hydrogenated and thus become more diffusive. For instance,

\[ \text{CH}_n(\text{ad}) + \text{H(free)} \rightarrow \text{CH}_{n+1}(\text{ad}) \quad (0 \leq n \leq 2) \]

\[ \text{O(ad)} + \text{H(free)} \rightarrow \text{OH(ad)} \]

\[ \text{C(ad)} + \text{OH(ad/free)} \rightarrow \text{COH(ad)} \]

\[ \text{CH}_n\text{OH(ad)} + \text{H(free)} \rightarrow \text{CH}_{n+1}\text{OH(ad)} \quad (0 \leq n \leq 1) \]

\[ \text{O(ad)} + \text{CH(ad/free)} \rightarrow \text{HCO(ad)} \]

\[ \text{O(ad)} + \text{COH(ad/free)} \rightarrow \text{COOH(ad)}. \]

In the interstellar medium, they can also be produced by UV photolysis or proton irradiation of grain ice mantles rich in H₂O, CO, CH₃OH and CH₄ [24,25].

The three issues to consider are reactivity, surface diffusion and hydrogenation. We find by calculation that the relevant surface chemistry is mostly driven by reactions involving radicals. When the adsorbate has a dangling bond, e.g. \( \text{CH}_n(1 \leq n \leq 2) \) or \( \text{CH}_n\text{OH}(0 \leq n' \leq 1) \), it usually remains chemisorbed after a–a or a–f recombinations which in most cases are devoid of activation barriers. For fully coordinated adsorbates, CH₃ and CH₂OH say, reaction with a second adsorbate implies bond substitution and thus detachment from the surface which depends on the chemisorption energy. It has been found by calculation that CH₃ and CH₂OH only chemisorb at site A with CAT Wiberg indices of 0.91 and 0.87, respectively, that are practically independent of surface model size. Therefore, surface diffusion for these two adsorbates is limited to thermal hopping whereby the chemical bond with the surface must be broken before displacement occurs. In Table 3

Table 3

<table>
<thead>
<tr>
<th>Chemisorption energies (eV) for CH₃ and CH₂OH</th>
<th>CAT</th>
<th>GA1</th>
<th>GA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>(-0.699)</td>
<td>(-0.255)</td>
<td>(-0.382)</td>
</tr>
<tr>
<td>CH₂OH</td>
<td>(+0.047)</td>
<td>(-0.333)</td>
<td>(-0.460)</td>
</tr>
</tbody>
</table>
we list their chemisorption energies obtained with the different surface models; it may be seen that the GA1 energies (\(E_A\)) are within \(-0.5 \leq E_A \leq -0.2\) eV and increase somewhat with surface size while CAT gives energies that are significantly different from GA1. By contrast, CH\(_n\) (\(1 \leq n \leq 2\)) and CH\(_n\)OH (\(0 \leq n \leq 1\)) chemisorb at both A and B sites, and therefore surface diffusion may take place without desorption. In Table 4 the chemisorption energy differences between sites A and B, \(\Delta E_{AB} \equiv E_A - E_B\), are given. For GA1, \(\Delta E_{AB}\) is not larger than 0.7 eV except for CH, and it decreases with surface size. The CAT absolute values are noticeably smaller than those for GA1. It may be noticed that in Tables 3,4 the CAT chemisorption energies for PAH2 and PAH3 are not listed; this is due to unreliable values when the larger surface models are used which are caused by inaccurate functionals in CATIVIC at large interatomic distances.

Chemisorption of the carboxylic group (COOH), as well as that of formyl (HCO), occurs in three modes (see Fig. 2): through both the C and O atoms, i.e. two-site chemisorption (mode M1); via the O atom alone (mode M2) and through the C atom (mode M3). Wiberg indices are given as an indication of bond strengths. It may be seen that the uncoordinated C atomic component in M2 is too high (3.3 Å above the surface level) for a–a reactions to occur, and M3 is fully coordinated due to the double C=O bond. Hence, M1 is the only adsorbate configuration of COOH (and of HCO) of interest in surface reactions because of its accessible and uncoordinated C component; furthermore, since M1 is doubly chemisorbed, it is not likely to diffuse and acts as a receptor for mobile adsorbates in polymerization.

In H-rich environments (hot molecular cores, for instance), display \(H_2\) number densities in the range \(10^{12} - 10^{14}\) m\(^{-3}\) and temperatures of 100–300 K), hydrogenation competes with surface diffusion limiting the size of the molecular synthesis end-products. If it dominates, step-by-step hydrogenation of the CH\(_n\) and C\(_n\)OH adsorbates ultimately leads to desorbed methane (CH\(_4\)) and methanol (CH\(_3\)OH), respectively. Hydrogenation of the formyl adsorbate in the M2 and M3 modes (i.e. singly chemisorbed through its O and C components, respectively) produces free formaldehyde (H\(_2\)CO) in a single step while in the case of M1 (two-site chemisorbed) it follows the progression:

\[
\begin{align*}
\text{HCO(\text{ad}) + H \rightarrow H_2\text{CO}(\text{ad})} & \quad (7) \\
\text{H}_2\text{C}(\text{ad}) + H \rightarrow \text{CH}_2\text{OH}(\text{ad}) & \quad (8) \\
\text{CH}_2\text{OH}(\text{ad}) + H \rightarrow \text{CH}_2\text{OH}(\text{free}). & \quad (9)
\end{align*}
\]

Similarly, in the case of the carboxylic M2 and M3 modes, a single hydrogenation yields free formic acid (HCOOH) while for M1 it takes the reaction route (see Fig. 3).

\[
\begin{align*}
\text{COOH(\text{ad}) + H \rightarrow HCOOH(\text{ad})} & \quad (10) \\
\text{HCOOH(\text{ad}) + H \rightarrow HOCHOH(\text{ad})} & \quad (11) \\
\text{HOCHOH(\text{ad}) + H \rightarrow CHOH(\text{free}) + H_2O(\text{free})}. & \quad (12)
\end{align*}
\]

Fig. 3a–b show that the Wiberg index \(I_w\) gives an indication of which bond is likely to be replaced by hydrogenation. In Fig. 3a, the weakest bond is that of the O atom to the surface \(I_w = 0.79\), and in Fig. 3b it is one of the two C–O bonds \(I_w = 0.79\). Although free CH\(_2\)(OH)\(_2\) (methanediol) can be produced in the final reaction step (12), the free radical CHOH can also be liberated which is bound to react with a neighboring adsorbate causing further processing, e.g. vinyl alcohol:

\[
\text{CH}_2(\text{ad}) + \text{CHOH(\text{free}) \rightarrow CH}_2 = \text{CHOH(\text{free}).} \quad (13)
\]

### Table 4

Differences in chemisorption energies (eV) between sites A and B (\(\Delta E_{AB}\)) for different adsorbate–substrate systems

<table>
<thead>
<tr>
<th>CAT</th>
<th>GA1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAH1</td>
</tr>
<tr>
<td>CH</td>
<td>-0.910</td>
</tr>
<tr>
<td>CH(_n)</td>
<td>0.119</td>
</tr>
<tr>
<td>COH</td>
<td>0.315</td>
</tr>
<tr>
<td>HCOH</td>
<td>0.533</td>
</tr>
</tbody>
</table>

4. Monocarboxylic acid chains

When the surface reaction rates become comparable to or greater than hydrogenation, the graphite surface becomes a fertile ground for organic synthesis. In the case of monocarboxylic chains, reaction pathways start with the carboxylic M1 adsorbate (see Fig. 2) which initiates polymerization by taking the role of a fixed receptor for mobile CH\(_n\) diffusors. The smallest two-carbon chain, namely acetic acid (CH\(_3\)COOH), is thus formed in reaction pathways of the type:

\[
\begin{align*}
\text{COOH(\text{ad}) + CH}_n(\text{free/\text{ad}) \rightarrow CH}_n\text{COOH(\text{ad})} & \quad (1 \leq n \leq 3) \quad (14) \\
\text{CH}_n\text{COOH(\text{ad}) + (3 - n)H \rightarrow CH}_2\text{COOH(\text{ad})} & \quad (1 \leq n \leq 3). \quad (15)
\end{align*}
\]

In the case of an a–a recombination with \(n \leq 2\) in reaction (14), the CH\(_n\) fragment remains bonded to both the substrate and the COOH with similar bond strengths, \(I_w \approx 0.91\) (see Fig. 4a). It is found by calculation that while the CH\(_n\) bond to the COOH adsorbate is always maintained during hydrogenation, the CH\(_n\) bond to the surface is broken during the last step \((n \rightarrow 3)\) detaching it from the surface thus impeding further polymerization. The final chemisorbed configuration of acetic acid is depicted in Fig. 4b, and as listed in Table 5, its geometry is found to be insensitive to surface model size. A comparison of data by CAT and GA1 indicates that bond lengths and bond angles are probably accurate to within 5% and 10%, respectively. Reactions (14) and (15) can be alternatively initiated by a formyl M1 adsorbate yielding acetaldehyde (CH\(_3\)CHO).
Successive hydrogenations of the COOH fragment within the CHₙCOOH adsorbate, instead of CHₙ as shown in reaction (15), can also take place following a series of steps similar to those in reactions (11) and (12), namely

\[ \text{CH}_n\text{COOH}(\text{ad}) + \text{H} \rightarrow \text{CH}_n(\text{HOCOH})(\text{ad}) \]  
\[ \text{CH}_n(\text{HOCOH})(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{COH}(\text{ad}) + \text{H}_2\text{O}(\text{free}) \]  
\[ \text{CH}_n\text{COH}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CHOH}(\text{ad}). \]

The option with \( n = 2 \) in step (18) is equivalent to chemisorbed vinyl alcohol while a further hydrogenation step with \( n = 3 \) produces free ethanol (CH₃CH₂OH).

If hydrogenation is much slower, further surface chemistry takes place leading to chain growth

\[ \text{CH}_n\text{COH}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CHO}(\text{ad}) + \text{H}_2\text{O}(\text{free}) \]  
\[ \text{CH}_n\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]  
\[ \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) + \text{H} \rightarrow \text{CH}_n\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}(\text{ad}) \]

In Fig. 5 we show the formation of a four-carbon chain with \( m = 2 \) and \( n = 0 \), i.e. solely built up from CH₃ monomers. It may be seen that the chain always remains

Table 5

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>CAT PAH1</th>
<th>PAH2</th>
<th>GA1 PAH1</th>
<th>PAH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d(O1C2S2) )</td>
<td>1.40</td>
<td>1.40</td>
<td>1.51</td>
<td>1.52</td>
</tr>
<tr>
<td>( d(C1C2S1) )</td>
<td>1.61</td>
<td>1.62</td>
<td>1.64</td>
<td>1.64</td>
</tr>
<tr>
<td>( d(C1O1C2) )</td>
<td>1.40</td>
<td>1.40</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>( d(C1C2S1) )</td>
<td>1.61</td>
<td>1.60</td>
<td>1.57</td>
<td>1.56</td>
</tr>
<tr>
<td>( d(O1C1C2S1) )</td>
<td>0.95</td>
<td>0.95</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>( d(C1C2S1) )</td>
<td>1.53</td>
<td>1.53</td>
<td>1.51</td>
<td>1.51</td>
</tr>
<tr>
<td>( d(C1C2H) )</td>
<td>1.11</td>
<td>1.11</td>
<td>1.09</td>
<td>1.09</td>
</tr>
<tr>
<td>( \angle(C1O1C2) )</td>
<td>104.5</td>
<td>104.5</td>
<td>116.8</td>
<td>116.9</td>
</tr>
<tr>
<td>( \angle(C1C2O2) )</td>
<td>108.1</td>
<td>107.9</td>
<td>107.8</td>
<td>107.7</td>
</tr>
<tr>
<td>( \angle(C1O1C2) )</td>
<td>109.4</td>
<td>109.3</td>
<td>111.5</td>
<td>111.3</td>
</tr>
<tr>
<td>( \angle(C1C2O2) )</td>
<td>116.7</td>
<td>116.1</td>
<td>108.2</td>
<td>108.9</td>
</tr>
<tr>
<td>( \angle(C1C2O2) )</td>
<td>111.8</td>
<td>111.2</td>
<td>112.2</td>
<td>112.6</td>
</tr>
</tbody>
</table>

Atomic labels as in Fig. 4b. Bond distances (Å) and angles in degrees.
chemisorbed through both the carboxylic head and the CH$_2$ tail end; moreover, the bond strengths of the former do not weaken during polymerization. The tail end is open to further polymerization unless it separates from the surface by reacting with a CH$_3$ monomer 

\[
\text{CH}_3(\text{CH}_2)_n\text{COOH(}\text{ad}) \rightarrow \text{CH}_3(\text{CH}_2)_{n+1}\text{COOH(}\text{ad})
\]

or becomes hydrogenated (see Fig. 5d) 

\[
\text{CH}_3(\text{CH}_2)_n\text{COOH(}\text{ad}) + \text{H} \rightarrow \text{CH}_3(\text{CH}_2)_{n+1}\text{COOH(}\text{ad}).
\]

A relevant point is that a chain built up only with CH$_2$ monomers, \(n = 0\), gives rise to the straight-chain isomer while if CH diffusors are involved, \(n > 0\), branching can occur. In contrast to CH$_2$, CH remains bonded to the surface during chain assembling thus creating a bifurcation point for a second branch of surface reactions.

Polymerization in Eqs. (19) and (20) can be alternatively seeded by HCO instead of COOH. For instance, a chemisorbed species of the 3-C propenal molecule (CH$_2$CHCHO) can be formed in a two-step process involving reaction (20) with \(m = n = 0\) and (19) with \(m = 0\) and \(n = 1\). Similarly, chemisorbed propanal (CH$_3$CH$_2$CHO) is produced by two reactions (19), the first with \(m = n = 0\) and the second with \(m = 1\) and \(n = 0\), followed by hydrogenation of the end monomer.

5. Polyl formation

The formation of sugars, sugar acids and alcohols is similar to that described for monocarboxylic acids in Section 4. It is found by calculation that polymerization is initiated by either the formyl or carboxylic group in the M1 two-site chemisorption mode (see Fig. 2), and is built up from diffusive adsorbates of the type CH$_n$OH (\(0 \leq n \leq 2\)). Polymer length depends again on the competition between surface diffusion and hydrogenation rates. For instance, the simplest two-carbon monosaccharide glyceraldehyde (CH$_2$OHCHO) can be formed in the two-step process

\[
\text{HCO(}\text{ad}) + \text{CH}_n\text{O(}\text{free/}\text{ad}) \rightarrow \text{CH}_n\text{OHCHO(}\text{ad})
\]

\(0 \leq n \leq 2\) (23)

\[
\text{CH}_n\text{OHCHO(}\text{ad}) + (2-n)\text{H} \rightarrow \text{CH}_2\text{OHCHO(}\text{ad})
\]

\(0 \leq n \leq 2\) (24)

As expected, the resulting adsorbate configuration, as shown in Fig. 6, is similar to that of acetic acid, and its geometry (see Table 6) is again practically independent of CH$_2$OHCHO.

Fig. 6. Glycolaldehyde molecule chemisorbed on the graphite plane.
Polymerization is initiated by either a carboxyl (COOH) or a formyl (HCO) group anchored to the surface through two chemisorption sites, and grows with mobile diffusors of the type CH$_n$ ($1 \leq n \leq 3$) and CH$_m$OH ($0 \leq m \leq 2$). In the case of monocarboxylic acid chains, CH$_n$ diffusors with $n = 2$ give rise to the straight-chain isomer while the involvement of those with $n = 1$ leads to branching. Polymerization is terminated by a CH$_3$ monomer or by detachment of the tail end from the surface due to hydrogenation.

Sugar polymerization relies on CH$_n$OH diffusors. A notable feature particular to sugar chains is that they display hydrogen bridge bonds that tend to increase curvature once the tail end is separated from the surface after hydrogenation. Moreover, further hydrogenations of the COOH or HCO polymer heads lead to the formation of alcohols.

The proposed surface recombination pathways have been validated by both semi-empirical and ab initio methods and by considering surface models of growing size. This latter aspect is shown to have some influence on chemisorption energies and diffusion barriers, particularly related to the extent of substrate reconstruction during adsorbate–substrate bonding. On the other hand, the determination of a more complete set of kinetic parameters would allow dynamical estimates of the speeds of these reaction pathways would imply lengthier calculations (e.g. transition states and frequency factors) and the introduction of additional numerical approaches. Furthermore, current lack of measurements for data validation would also compromise the reliability of such estimates.

With regards to carboxylic acid surface polymerization, it is found, in agreement with experiment [10], that chains grow parallel to the surface. Since they are chemisorbed through their COOH heads, desorption would then be the result of the competition between the two surface bonds and the formation of the C=O double bond. It is also shown that both straight- and branched-chain isomers can be formed. Since both types have been detected in chondritic meteorites [7,8], this finding emphasizes the importance of measuring their relative concentrations as it would provide indications of the relative abundances and mobilities of the CH and CH$_2$ diffusors. Also, the observed logarithmic abundance decrease with increasing carbon number in the meteoritic chains appears to fit the proposed stepwise surface polymerization.

Present results allow inferences which may be of astrochemical interest. For instance, we show that for surface diffusion to take place on a graphite surface, relatively high surface temperatures ($T \geq 100$ K) are required to overcome energy barriers, and diffusion rates should in principle increase with surface temperature. This finding is of arguable relevance in the explanation of the observations of complex saturated organic molecules in the interstellar medium which are exclusively attributed to hot molecular cores, and in the increase in abundances for most species with grain temperature [26,27]. Although the present scheme can account for the synthesis of a large number of observed C$_5$O$_2$H$_2$ molecules, there are many that do

---

**Table 6**

<table>
<thead>
<tr>
<th></th>
<th>CAT PAH1</th>
<th>CAT PAH2</th>
<th>GA1 PAH1</th>
<th>GA1 PAH2</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(O$^1$C$^{S_2}$)</td>
<td>1.40</td>
<td>1.41</td>
<td>1.59</td>
<td>1.53</td>
</tr>
<tr>
<td>d(C$^{S_1}$C$^{S_1}$)</td>
<td>1.59</td>
<td>1.60</td>
<td>1.59</td>
<td>1.58</td>
</tr>
<tr>
<td>d(C$^{O_1}$O$^{S_1}$)</td>
<td>1.38</td>
<td>1.38</td>
<td>1.51</td>
<td>1.51</td>
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<tr>
<td>d(C$^{S_1}$C$^{S_1}$C$^{S_1}$)</td>
<td>1.61</td>
<td>1.58</td>
<td>1.57</td>
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<tr>
<td>d(C$^{H_1}$H$^{O_2}$)</td>
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<td>1.14</td>
<td>1.09</td>
<td>1.09</td>
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<tr>
<td>d(C$^{O_1}$C$^{S_1}$)</td>
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<td>1.53</td>
<td>1.53</td>
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<td>d(C$^{O_1}$O$^{S_1}$)</td>
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<td>1.45</td>
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<tr>
<td>d(C$^{H_1}$H$^{O_2}$)</td>
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<td>1.13</td>
<td>1.09</td>
<td>1.09</td>
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<tr>
<td>d(O$^{H_1}$H$^{O_2}$)</td>
<td>0.95</td>
<td>0.95</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Atomic labels as in Fig. 6. Bond distances ($d$) in Å and angles in degrees.

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Surface model size. The CAT bond lengths are consistently smaller than GA1 (by 3%) while the bond angles are somewhat larger but they agree to within 10% and 15%, respectively. If two additional hydrogenation steps are considered in reaction (24), free ethylene glycol (HOCH$_2$CH$_2$OH) is produced.

If the hydrogenation step (24) is delayed, further polymerization is promoted by surface reactions of the type

$$(\text{CHOH})_m(\text{COOH})_n\text{CHO(ad)} + \text{CHOH(free/ad)}$$

$\rightarrow (\text{CHOH})_{m+1}(\text{COOH})_n\text{CHO(ad)} \quad (25)$$

$$(\text{CHOH})_m(\text{COOH})_n\text{CHO(ad)} + \text{COH(free/ad)}$$

$\rightarrow (\text{CHOH})_m(\text{COOH})_{n+1}\text{CHO(ad)}. \quad (26)$$

Sugar alcohols (e.g. glycerol) can be generated in reaction (25) with $n = 0$ and $1 \leq m \leq 4$, desorbing after a threefold hydrogenation of the end monomers. Sugar acids (e.g. glycercic acid) are formed in reaction (25) if the HCO initiator is replaced by COOH, with $n = 0$ and $1 \leq m \leq 4$ and a single terminal hydrogenation. In the dicarboxylic sugar acid variant, polymerization with $n = 0$ and $2 \leq m \leq 4$ is brought to a halt by a second chemisorbed carboxyl group. The deoxy sugar acids, on the other hand, include a mixture of diffusors of the type CHOH, CH$_2$ and CH$_3$COH.

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**6. Summary and discussion**

Extensive quantum chemical calculations have been carried out to study the hetero catalytic capabilities of the graphite surface in the synthesis of carboxylic acid chains and polyols. Surface recombinations involve small functional groups, and it has been shown within the present model that molecular complexity depends on the dominance of surface diffusion over hydrogenation.
not fit its requirements. The most eminent case is methyl formate which is apparently formed by channels that do not involve a–a recombinations. Its relatively high abundance can then be interpreted as a measure of the slowness of a–a recombinations relative to hydrogenations. Further studies of the surface chemistry of methyl formate are currently in progress encouraged by the poor performance of gas-phase reactions in reproducing the observed abundances [28].

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References