Supplement of

Collision-sticking rates of acid–base clusters in the gas phase determined from atomistic simulation and a novel analytical interacting hard-sphere model

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Calculated potential of mean force (PMF) curves for acid-base clusters

Figure S1. Potentials of Mean Force as a function of the center of mass distance between the investigated acid-base “monomers” in Hamaker’s approach, obtained from well-tempered metadynamics simulations at T=300 K using an OPLS-AA force field.

Extracted $\epsilon$ and $\sigma$ values from the calculated PMF curves

Table S1. Extracted $\epsilon$ and $\sigma$ values

<table>
<thead>
<tr>
<th></th>
<th>$(\text{CH}_3)_2\text{NH} &amp; (\text{CH}_3)_2\text{NH}$</th>
<th>$\text{H}_2\text{SO}_4 &amp; \text{H}_2\text{SO}_4$</th>
<th>$\text{H}_2\text{SO}_4 &amp; (\text{CH}_3)_2\text{NH}$</th>
<th>$\text{H}_2\text{SO}_4 &amp; \text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+$</th>
<th>$(\text{CH}_3)_2\text{NH} &amp; \text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$ [eV]</td>
<td>$\sim 0$</td>
<td>0.29</td>
<td>0.26</td>
<td>0.93</td>
<td>0.35</td>
</tr>
<tr>
<td>$\sigma$ [Å]</td>
<td>N/A</td>
<td>3.71</td>
<td>3.54</td>
<td>3.19</td>
<td>3.36</td>
</tr>
</tbody>
</table>
Two example cases where the interacting hard-sphere model and the central field approach result in significantly different critical impact parameters

**Figure S2.** Critical impact parameter for collisions of carbon dioxide monomers at 100 K. The Lennard-Jones parameters are $\epsilon = 0.0108$ eV and $\sigma = 3.04$ Å.

**Figure S3.** Critical impact parameter for collisions of water monomers at 250 K. The Lennard-Jones parameters are $\epsilon = 0.031$ eV and $\sigma = 2.928$ Å.
The root of Eq. 14 in the main text

In this part, we provide a reasoning to the statement that Eq. 14 in the main text always has exactly one real root that is larger than $R_c$, and we shall identify that root. Substitution of Eq. 13 in the main text into $\omega_v(r)$ yields:

$$\omega_v(r, U_{mc}) = r^2 \left[ 1 + \frac{8n_c e \sigma^6}{\mu v_0^2} \cdot \frac{1}{(r^2 - R_c^2)^3} \right]. \quad (S1)$$

We take the derivative of Eq. S1 with respect to $r$ and obtain:

$$\omega'_v(r, U_{mc}) = 2r \left[ 1 - \frac{8n_c e \sigma^6}{\mu v_0^2} \cdot \frac{2r^2 + R_c^2}{(r^2 - R_c^2)^3} \right] \equiv 2r[1 - \theta f(r)], \quad (S2)$$

where, $\theta = \frac{8n_c e \sigma^6}{\mu v_0^2}$ is a positive constant and

$$f(r) = \frac{2r^2 + R_c^2}{(r^2 - R_c^2)^3} = \frac{2}{(r^2 - R_c^2)^3} + \frac{3R_c^2}{(r^2 - R_c^2)^4} \quad (S3)$$

decreases monotonically from $+\infty$ to 0 as $r$ increases from $R_c$ to $+\infty$. Therefore, $\omega'_v(r, U_{mc}) = 0 \iff f(r) = \frac{1}{\theta}$ should have a single root for $r > R_c$. Note that $\omega'_v(r, U_{mc}) = 0$ is equivalent to Eq. 14 in the main text, so now it is safe to say that Eq. 14 has a single real root larger than $R_c$. This single real root $R_m$ should correspond to the maximum of the four roots of the quartic function defined by Eq. 14, which is:

$$R_m^2 = -\frac{a_3}{4a_4} + M + \frac{1}{2} \sqrt{-4M^2 - 2p + \frac{q}{M}}, \quad (S4)$$

where $p = \frac{8a_3 a_2^3 - 3a_2^2}{8a_4^2} = 0$, $q = \frac{a_3^3 - 4a_3 a_2 a_1 + 8a_4^2 a_1}{8a_4^3} = -2l_c^6$, $M = \frac{1}{2} \sqrt{-\frac{2}{3}p + \frac{1}{3a_4}(N + \frac{\Delta_0}{N})}$, $N = \sqrt[3]{\frac{\Delta_1 + \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2}}$, $\Delta_0 = a_2^2 - 3a_3 a_1 + 12a_4 a_0 = -36R_c^2 l_c^6$, and $\Delta_1 = 2a_2^3 - 9a_3 a_2 a_1 + 27a_3^2 a_0 + 27a_1^2 a_4 - 72a_4 a_2 a_0 = 108l_c^{12}$ with $l_c \equiv \left( \frac{8n_c e \sigma^6}{\mu v_0^2} \right)^{\frac{1}{6}}$. Substituting the expressions of coefficients $a_i$ into Eq. S4 and rearranging leads to Eq. 15 in the main text.
Temperature dependence of collision and sticking rates for clusters of different sizes

**Figure S4.** Temperature dependence of collision (CR) and sticking rates (SR) for $\text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16, \text{and} \ 32$).

**Figure S5.** Temperature dependence of collision (CR) and sticking rates (SR) for $(\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n$ collisions ($n = 1, 2, 4, 8, 16, \text{and} \ 32$).
When the temperature is increased, the Maxwell Boltzmann distribution is shifted to higher speeds, which has two consequences: First, the monomer flux per unit collision cross section is increased due to higher average relative velocities. Second, the area of the collision cross section is decreased due to the diminished influence of the attractive forces at higher relative velocities. The rate of collision and sticking is hence the net effect of the above two competing factors. The second factor (i.e., decreased collision cross section due to increased temperature) is more significant for small clusters, as the attractive forces play a greater role (leading to higher collision enhancement factors). Therefore, the collision rate decreases with temperature for small clusters, while it increases with temperature for larger clusters.

For \( \text{H}_2\text{SO}_4 + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n \) collisions, the temperature dependence of the collision and sticking rates are similar, as the mass accommodation coefficient is always close to 1 in the studied temperature range. For \( (\text{CH}_3)_2\text{NH} + [\text{HSO}_4^- \cdot (\text{CH}_3)_2\text{NH}_2^+]_n \) collisions, the mass accommodation coefficient decreases sharply with temperature, hence the sticking coefficient also drops sharply with temperature.

**Step-by-step procedure for implementing the interacting hard-sphere model**

**Step 1. Input parameters to supply**

As input parameters for the interacting hard-sphere model, we need the energy \( \varepsilon \) and length \( \sigma \) Lennard-Jones self-interaction parameters and the radius \( R \) for each molecule in the collision system. For a collision between two molecules, this means the \( \varepsilon, \sigma, \) and \( R \) of each of these molecules. For a collision between a molecule and a cluster, this means the \( \varepsilon, \sigma, \) and \( R \) of each type of monomer in the cluster, as well as the molecule colliding with the cluster.

The Lennard-Jones self-interaction parameters can be obtained from literature (e.g., the following references\(^3\)-\(^7\)), potential of mean force calculations (as is done in the main text) or fitting to experimental or quantum chemistry data.

The radii of the molecules can be obtained from literature, calculated from liquid bulk density, or taken as the radius of gyration.

The radius \( R_c \) of a cluster consisting of \( N_t \) different types of monomers can be roughly, but sufficiently, estimated from the density \( \rho_i \) and molecular mass \( m_i \) of each monomer type in the cluster by assuming spherical monomer volumes:

\[
R_c = \left( \frac{3}{4\pi} \sum_{i}^{N_t} n_{c,i} m_i / \rho_i \right)^{1/3},
\]

where \( n_{c,i} \) is the number of monomers of type \( i \) in the cluster.
Step 2. Calculating the collision cross section

Molecule-molecule collision

We first need to calculate the distance $R_m$.

$$R_m = \sigma \left(\frac{16\epsilon}{\mu v_0^2}\right)^{1/6}, \quad (S6)$$

where $\mu$ is the reduced mass of the collision system. Depending on the relative magnitude of $R_m$ and the sum of hard-sphere radii of the two colliding molecules $R_i + R_j$, the collision cross section is calculated from one of the following equations:

$$\Omega(v_0) = \begin{cases} 
3\pi \sigma^2 \left(\frac{2\epsilon}{\mu v_0^2}\right)^{1/3}, & \text{if } R_m > R_i + R_j \\
\pi (R_i + R_j)^2 \left[1 + \frac{8\epsilon}{\mu v_0^2} \left(\frac{R_i + R_j}{\sigma}\right)^{-6}\right], & \text{if } R_m \leq R_i + R_j
\end{cases} \quad (S7)$$

Molecule-cluster collision

We consider collisions between a molecule and a cluster consisting of $N_t$ different types of monomers. First, we need to calculate the distance $R_m$.

$$R_m^2 = R_c^2 + M + \sqrt{-M^2 - \frac{q}{4M}}, \quad (S8a)$$

where

$$q = -2l_c^6, \quad (S8b)$$

$$M = \frac{\sqrt{(N+\Delta_0/N)/3}}{2}, \quad (S8c)$$

$$N = \left[\frac{\Delta_1 + \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2}\right]^{1/3}, \quad (S8d)$$

$$\Delta_0 = -36R_c^2 l_c^6, \quad (S8e)$$

$$\Delta_1 = 108l_c^{12}, \quad (S8f)$$

$$l_c = \left(\frac{8\epsilon}{\mu v_0^2} \sum_{i=1}^{N_t} \sigma_i^6 n_i \epsilon_i\right)^{1/6}. \quad (S8g)$$

Note that the equation of $l_c$ simplifies to $l_c = \left(8n_c \epsilon \sigma^6 / \mu v_0^2\right)^{1/6}$ as in the main text if the cluster consists of a single type of monomer.
Depending on the relative magnitude of $R_m$ and the sum of hard-sphere radii of the colliding molecule and cluster $R_i + R_j$, the collision cross section is calculated from one of the following equations:

\[
\Omega(v_0) = \begin{cases} 
\pi R_m^2 \left[ 1 + \frac{8}{\mu v_0^2 (R_m^2 - R_c^2)^3} \sum_{i=1}^{N_i} n_{c,i} \varepsilon_i \sigma_i^6 \right], & \text{if } R_m > R_i + R_j \\
\pi (R_i + R_j)^2 \left[ 1 + \frac{8}{\mu v_0^2 ((R_i + R_j)^2 - R_c^2)^3} \sum_{i=1}^{N_i} n_{c,i} \varepsilon_i \sigma_i^6 \right], & \text{if } R_m \leq R_i + R_j
\end{cases}
\]  

(S9)

Step 3. Calculating the collision rate coefficient

The collision rate coefficient is given by

\[
k_{\text{IHS}} = \int_0^{\infty} v_0 f_{\text{MB}}(v_0) \Omega(v_0) dv_0 \approx \sum_{v_0=0} v_0 f_{\text{MB}}(v_0) \Omega(v_0) \Delta v_0.
\]

(S10)

where $\Omega(v_0)$ is either the molecule-molecule or molecule-cluster collision cross section calculated in step 2, and $f_{\text{MB}}(v_0)$ the Maxwell-Boltzmann relative speed distribution

\[
f_{\text{MB}} = 4\pi v_0^2 \left( \frac{\mu}{2\pi k_B T} \right) \frac{3}{2} e^{-\frac{\mu v_0^2}{2k_B T}}.
\]

(S11)

Here, $k_B$ is the Boltzmann constant. When approximating $k_{\text{IHS}}$ as a sum, the sum should run over a relative range of $v_0$ according to the Maxwell-Boltzmann relative speed distribution (e.g., for collisions between H$_2$SO$_4$ with [HSO$_4$·(CH$_3$)$_2$NH$_3$]$^+$, the range $v_0 = 0$-850 ms$^{-1}$ covers more than 99.9% of the Maxwell-Boltzmann relative speed distribution at 300 K). Practically, the sum can be calculated numerically with an if statement in the code to distinguish between the two cases $R_m > R_i + R_j$ and $R_m \leq R_i + R_j$. 

8
References


