brief communications

Table 1 Product yields from different lithium compounds

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>Solvent</th>
<th>B</th>
<th>Organof-F yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiPF₄</td>
<td>EC</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>LiPF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Li[(CF₃SO₂)₂N]</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiMnO₄</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiNO₂</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>LiBF₄</td>
<td>EC + DMC</td>
<td>LiCoO₂</td>
<td>35</td>
</tr>
</tbody>
</table>

Yields of fluoro-organics are shown for ethylene carbonate reacting with lithium compounds A and B at 240 °C for 30–60 min in different solvents. EC, ethylene carbonate; DMC, dimethyl carbonate.

and their failure rate has dropped to about 0.3 per million. The consequences of runaway reactions have so far focused mainly on the risks of fire, burns and the release of hydrogen fluoride.

The compound 2-fluoroethanol is highly toxic (the 50%–lethal dose, LD₅₀, in mice is 0.1 mg kg⁻¹) and is readily formed by nucleophilic attack of fluoride ion on ethylene carbonate. Although no example of electrophilic fluorination using coordination anions such as LiPF₆ is known, we investigated whether a similar reaction could occur by this route.

Ethylene carbonate and LiPF₆ alone do not form fluoro-organics, but these are generated in abundance when any of the positive-electrode materials (LiₓMO₂, where M is Co, Ni or Mn) is also present. Gas chromatography with mass spectrometry (110 mass units) indicates that the fluoroethanol ether is formed under these conditions: two moles of ethylene carbonate react with one mole of LiPF₆ to yield one mole each of (FCH₂CH₂)₂O, LiF and bonded fluorine (CF₃⁻). The carbon anion with covalently bound fluorine (CF₃⁻) is inert.

The compound bis-(2-fluoroethoxy)ethane forms under these conditions: two moles of ethylene carbonate and one mole of LiPF₆ are consumed. The reaction with LiBV₄ produces volatile POF₃ (boiling point, 39.7 °C), representing 80% of the total fluoro-chemistry (110 mass units) indicates that the gas chromatography with mass spectrometry (110 mass units) indicates that the gas evolution of the chemicals evolved in runaway reactions have so far focused mainly on the risks of fire, burns and the release of hydrogen fluoride.

Table 1 Product yields from different lithium compounds

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>Solvent</th>
<th>B</th>
<th>Organof-F yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiPF₄</td>
<td>EC</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>LiPF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Li[(CF₃SO₂)₂N]</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiMnO₄</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiNO₂</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>LiBF₄</td>
<td>EC + DMC</td>
<td>LiCoO₂</td>
<td>35</td>
</tr>
</tbody>
</table>

Yields of fluoro-organics are shown for ethylene carbonate reacting with lithium compounds A and B at 240 °C for 30–60 min in different solvents. EC, ethylene carbonate; DMC, dimethyl carbonate.

and their failure rate has dropped to about 0.3 per million. The consequences of runaway reactions have so far focused mainly on the risks of fire, burns and the release of hydrogen fluoride.

The compound 2-fluoroethanol is highly toxic (the 50%–lethal dose, LD₅₀, in mice is 0.1 mg kg⁻¹) and is readily formed by nucleophilic attack of fluoride ion on ethylene carbonate. Although no example of electrophilic fluorination using coordination anions such as LiPF₆ is known, we investigated whether a similar reaction could occur by this route.

Ethylene carbonate and LiPF₆ alone do not form fluoro-organics, but these are generated in abundance when any of the positive-electrode materials (LiₓMO₂, where M is Co, Ni or Mn) is also present. Gas chromatography with mass spectrometry (110 mass units) indicates that the fluoroethanol ether is formed under these conditions: two moles of ethylene carbonate react with one mole of LiPF₆ to yield one mole each of (FCH₂CH₂)₂O, LiF and bonded fluorine (CF₃⁻). The carbon anion with covalently bound fluorine (CF₃⁻) is inert.

The compound bis-(2-fluoroethoxy)ethane forms under these conditions: two moles of ethylene carbonate and one mole of LiPF₆ are consumed. The reaction with LiBV₄ produces volatile POF₃ (boiling point, 39.7 °C), representing 80% of the total fluoro-chemistry (110 mass units) indicates that the gas chromatography with mass spectrometry (110 mass units) indicates that the gas evolution of the chemicals evolved in runaway reactions have so far focused mainly on the risks of fire, burns and the release of hydrogen fluoride.

Table 1 Product yields from different lithium compounds

<table>
<thead>
<tr>
<th>Run</th>
<th>A</th>
<th>Solvent</th>
<th>B</th>
<th>Organof-F yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiPF₄</td>
<td>EC</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>LiPF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Li[(CF₃SO₂)₂N]</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiCoO₂</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiMnO₄</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>LiBF₄</td>
<td>EC</td>
<td>LiNO₂</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>LiBF₄</td>
<td>EC + DMC</td>
<td>LiCoO₂</td>
<td>35</td>
</tr>
</tbody>
</table>

Yields of fluoro-organics are shown for ethylene carbonate reacting with lithium compounds A and B at 240 °C for 30–60 min in different solvents. EC, ethylene carbonate; DMC, dimethyl carbonate.

extreme caution and only where ad hoc facilities are available.

Amer Hammani, Nathalie Raymond, Michel Armand

Laboratoire International sur Les Matériaux Electro-actifs CNRS-UdM, UMR 2289, Université de Montréal, P.O. Box 6122, Montréal, Québec H3C 3J7, Canada

e-mail: michel.armand@umontreal.ca

Competing financial interests: declared none.

Electro-Actifs CNRS-UdM, UMR 2289, Laboratoire International sur Les Matériaux Electro-actifs CNRS-UdM, UMR 2289, Université de Montréal, P.O. Box 6122, Montréal, Québec H3C 3J7, Canada

e-mail: michel.armand@umontreal.ca

Palaeontology

Spider-web silk from the Early Cretaceous

The use of viscous silk in aerial webs as a means to capture prey was a key innovation of araneoid spiders and has contributed largely to their ecological success. Here I describe a single silk thread from a spider’s web that bears glue droplets and has been preserved in Lebanese amber from the Early Cretaceous period for about 130 million years. This specimen not only demonstrates the antiquity of viscous silk and of the spider superfamily Araneoidae, but is also some 90 million years older than the oldest viscous spider thread previously reported in Baltic amber from the Eocene epoch.

The silk glands that produce the glue coating on viscous silk may be the best single character to define the Araneoidae, the superfamily that includes all orb-weavers and the comb-footed spiders (Theriidae)³. A fossil spider from the Early-Middle Jurassic (which is about 190 Myr old) has been described — on the basis of characters other than its silk-producing glands — as belonging to the Araneoidae, and araneoid spiders have been recorded from the Early Cretaceous⁴.⁵

Spiders are known to have been able to produce silk since the Mid-Devonian period, about 410 Myr ago. It is unclear, however, how today’s silk-producing aerial webs with viscous silk evolved from the probably primitive silk that was used by Devonian spiders. Current ideas about the evolution of aerial webs and of viscous silk are based on the phylogeny of the spiders, which in turn is based on morphological characters — mostly genitalic ones — whose evolution is generally not directly linked to the spider’s ability to build webs or to produce viscous silk.

The present specimen (C19/2, held at the Staatliches Museum für Naturkunde in Stuttgart, Germany) was collected by Dieter Schiele in 1969 from amber beds located near Jezzine in Lebanon. These deposits are dated to the Hauterivian (about 127–132 Myr ago) and represent the oldest known amber with insect inclusions.

The specimen contains a single thread of about 4 mm in length, which shows a striking resemblance to recent araneoid spider threads, with 38 distinct fossilized glue droplets arranged at regular intervals along two sections (Fig. 1a). The thread diameter (3 μm) and the size (7–29 μm), density (22 droplets per mm), arrangement (small droplets alternating with larger ones) and shape (semi-transparent, globules, slightly elongated along the thread) of most glue droplets (Fig. 1b) closely match those in recent araneoid webs⁶. Some droplets have a larger diameter of up to 85 μm (Fig. 1c), probably as a result of water uptake from the resin (araneoid glue droplets are highly hydroscopic⁷) and subsequent merging with neighbouring droplets.

As the specimen contains only a single thread, we cannot identify with certainty the type of web of which this thread was a part. It may have been part of an orb-web or of a gum-footed web, as built by some

![Figure 1](image_url)
recent theridiid spiders. In these webs, only the gumfeet, the peripheral parts of the threads extending from a central structure to the substrate, are equipped with glue droplets.

It is likely that the present specimen was such a gumfoot, because viscid threads in other araneoid webs are always surrounded by non-sticky threads, and because gumfeet are the only type of viscid thread that is built near the bark of a tree, where the probability of becoming engulfed in resin is largest. In addition, the thread is only partly covered with glue droplets, another feature that it shares only with gumfeet.

However, the fossil thread could have been part of a web type that no longer exists today. In any case, the present specimen is direct evidence for the antiquity of viscid spider silk and provides independent evidence for the antiquity of the Araneidae.

### Samuel Zschokke

Department of Integrative Biology, Section of Conservation Biology, University of Basel, 4056 Basel, Switzerland
e-mail: samuel.zschokke@alumni.ethz.ch


### Competing financial interests: declared none.

#### Insect signalling

### Components of giant hornet alarm pheromone

Up to 74 people die each year in Japan after being stung by Hymenopteran insects, with hornets (Vespa spp.) being among the worst offenders. Here we identify a volatile, multi-component alarm pheromone in the venom of the world's largest hornet, V. mandarinia, and use field bioassays to show that 2-pentanol is its principal active component, and that 3-methyl-1-butanol and 1-methylbutyl-3-methylbutanoate act synergistically with it. The compound 1-methylbutyl-3-methylbutanoate, which may also be a foraging-site-marking pheromone, elicits a strong defensive reaction in the sympatric prey V. simillima xanthoptera; the behaviour is identical to the defensive reaction by V. simillima when it detects the foraging-site-marking pheromone secreted by V. mandarinia scouts. This 'kairemone' detection is an example of adaptation to predation by sympatric species.

The synergistic interaction and the kairemonal function described here indicate that hornets probably use semiochemicals in a complex form. Single-component alarm pheromones are found in the venom of other insects (for example, 2-methyl-3-butanol-2-ol in Vespa crabro, N-(3-methylbutyl)acetamide in Vespula squamosa and (25,6R,8S)-2,8-dimethyl-1,7-dioxaaspiro[5.5]undecane in Polybia occidentalis).

A preliminary analysis of the volatile components in venom from all seven Japanese hornet species confirms that they contain alcohols and esters that are also common in manufactured food and cosmetic products (our unpublished results). It may therefore be sensible to screen these commercial products for the presence of the following chemicals:

4. (R)-2-pentanol; 5. (±)-2-pentanol; 6. 3-methyl-1-butanol; 7. (S)-1-methylbutyl-3-methylbutanoate; 8. (R)-1-methylbutyl-3-methylbutanoate; 9. (±)-1-methylbutyl-3-methylbutanoate; 10. (±)-2-pentanol and (±)-1-methylbutyl-3-methylbutanoate; 11. (±)-1-methylbutyl-3-methylbutanoate and 3-methyl-1-butanol; 12. (±)-2-pentanol and 3-methyl-1-butanol; 13. (S)-2-pentanol, 3-methyl-1-butanol and (±)-1-methylbutyl-3-methylbutanoate. Venom extract and 2-pentanol each elicited a defensive reaction, which increased when the filter paper was impregnated with all three volatile components. Data are mean responses ± s.d. (five replicates); letters indicate a significant difference (P < 0.01) by Tukey's test.