Chemistry Chat

Nine Short Stories - Part 1 -

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The university laboratory is a treasure trove of failures, errors and mistakes, and these provide useful information for students to improve experimental techniques. I would like to write nine short stories in three installments. I hope that even one of them will be helpful to students. This time, I will talk about solvents.

Story 1. Sudden appearance of an ethyl group

Fumiko conducted a reaction that was monitored using thin-layer chromatography (TLC). As the reaction proceeded, the spot for the starting material gradually disappeared and new spots due to different products appeared. Fumiko removed the solvent under reduced pressure and measured the ^{1}H NMR spectrum of the residue. When she looked at the spectrum, she was very surprised by signals due to a ethyl group, since she did not use any reagent containing an ethyl group. It was quite strange. Hence she went to the professor's office, and asked for advice. The professor said, "Did you use chloroform as a solvent? When she answered "yes", he said "I knew it". However, Fumiko had no idea what he was talking about.

⇨ Halogen-containing solvents such as chloroform are quite restricted industrially due to their toxicity. Nevertheless, it is a competent solvent and is still used in university laboratories. It can also cause some unusual reactions. One of the causes is the small amount of acid it contains. The other is **ethanol, which is added as a stabilizer**, preventing it from decomposing and producing phosgene. Ethanol is a highly reactive compound, which sometimes **participates in the reaction**. This can lead to confusion when an unfamiliar signal appears

Story 2. Different compounds in different solvents

Mizuki synthesized a hitherto unknown compound and collected the spectral data. When he measured the ^{1}H NMR spectrum using chloroform-*d*, he observed signals consistent with the structure of the target compound. However, the solubility of the compound in chloroform-*d* was not high enough to measure the ^{13}C NMR spectrum. Therefore, he measured the ^{13}C NMR using deuterated dimethyl sulfoxide (DMSO-d_6). However, the obtained data were inconsistent with the expected structure, which left him confused. Also, when he measured the ^{1}H NMR spectrum using DMSO-d_6, he observed quite different signals from those obtained using chloroform-*d*.

⇨ DMSO is a highly polar solvent and will dissolve many polar compounds, but it is difficult to evaporate because of its high boiling point. For NMR measurements, relatively inexpensive chloroform-*d* is usually employed as the solvent. DMSO-d_6 is used in the case of poorly soluble compounds. However, it is a misconception that just dissolving the compound in the solvent causes no change in the structure of the compound. **The structure sometimes changes (or reacts) when the surrounding polarity changes**. You should measure NMR spectra in each solvent to avoid troublesome mistakes. If you notice such small changes, you might be able to develop new projects.

Story 3. Crystals that appear and disappear

One day in the rainy season just before summer, Fumiko was filtering a diethyl ether solution using folded filter paper. The filtration was going well, but during the process, she observed beautiful colorless crystals on the edge of the filter paper. Crystals draw much attention from all chemists. Fumiko tried to remove the crystals with a spatula, but they disappeared the moment she scooped them up. However, the crystals reappeared on the filter paper as if in derision. It is human nature to want to chase after something that is not easily obtained. After that, Fumiko tried again and again to gather the crystals, but in the end her efforts were not fruitful.

⇨ Diethyl ether is a low boiling point, high-volatility organic solvent. When filtering on a hot and humid day, it rapidly volatilizes from the large surface area of the filter paper. In that case, it absorbs vaporization heat from the surroundings, so the moisture in the air will condense on the filter paper. That's right, what Fumiko was trying to remove were **ice crystals**. It is natural for them to appear immediately, but when you try to collect them, they rapidly disappear. But the desire to discover something new is a necessary attitude in research.

Professor Nagatoshi Nishiwaki received a Ph.D. in 1991 from Osaka University. He worked in Professor Ariga's group in the Department of Chemistry, Osaka Kyoiku University, as an assistant professor (1991-2000) and associate professor (2001-2008). From 2000 to 2001, he was with Karl Anker Jørgensen's group at Århus (Aarhus) University in Denmark. He worked at the Center for Collaborative Research, Anan National College of Technology as an associate professor from 2008 to 2009. Then, he moved to the School of Environmental Science and Engineering, Kochi University of Technology in 2009, where he has been a professor since 2011. His research interests comprise synthetic organic chemistry using nitro compounds, heterocycles (synthesis, ring transformation, 1,3-dipolar cycloaddition, application as tools in organic synthesis), pseudo-intramolecular reactions, and solid-supported palladium catalysts.