Standard Operating Procedure

Task: Benzophenone Ketyl Radical Recipe
Date: 5/25/2013
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Background:

- Benzophenone ketyl radical is an excellent water indicator for many organic solvents. When water reacts with the purple ketyl radical, a color change to blue and eventually colorless is observed. The test solution described here is designed for testing aliquots of solvent in the glovebox to determine the amount of water in the range of ~10 ppm or less. A full derivation, courtesy of Prof. Theo Agapie (Caltech), is provided below.

Training Requirements:

- Lab safety training
- Glovebox training
- Pyrophoric chemical training

Potential Hazards:

- Pyrophoric sodium metal (perform in glovebox)

Materials Needed:

- Sodium metal
- Benzophenone
- THF
- 20 mL vial
- Magnetic stir bar

Procedure:

- In the glovebox, weigh 28 mg (1.22 mmol, 1.6 equiv) sodium metal into a 20 mL scintillation vial. Weigh pristine metallic sodium. Avoid the white oxide layer by cutting away the outer part of the sodium chunk. You can use a spatula (dedicated to be used **only** for sodium) to transfer the sodium metal.
- Add 0.137 g (0.752 mmol) benzophenone (Ph_2CO) to the vial.
- Dissolve in 20 mL THF and add a magnetic stir bar.
- Stir vigorously overnight.
- The clear, colorless solution should darken steadily to a blue color before eventually turning inky purple.
- The excess sodium will keep the indicating solution active and accurate for longer.

Using the test solution:

- Fill a small vial with about 4 mL of halogen-free, aprotic solvent (<u>see restrictions below</u>).
- Add one drop of the purple ketyl radical solution to the vial, using a long Pasteur pipet.
- Shake the vial to mix: if the color stays **purple** the solvent contains $< \sim 10$ ppm H_2O (it will lighten; a reddish color is OK). If the color turns **blue**, there is some water present. If the color fades entirely, there is a lot of water present.

- If the indicator does not remain purple after addition, add more purple ketyl radical solution **drop by drop** until the solution stays purple.
- For most solvents, the solution should maintain a purple color with 1 drop of ketyl radical solution. The number of drops added to the solvent corresponds to how much water is in solution. If a low water content is desired, test to maintain the purple color with 1 drop of solution.
- Note that THF is very difficult to dry: using 2 drops of solution to retain the purple color is satisfactory. All other solvents should maintain purple color with 1 drop of solution.
- The ketyl radical is also O_2 sensitive, so if a solvent fails the test, try degassing it. If the solvent fails the test, replace the solvent.
- Remember to test the solvent often (every 6 months as a general suggestion, test more/less often depending on your chemistry's sensitivity to water and O_2) and replace the solvent when it fails the ketyl radical test.

Solvent restrictions:
- Suitable solvents: pentane, hexanes, benzene, toluene, diethyl ether, tetrahydrofuran
- **Do not test** the following solvents: chlorinated (e.g. CH_2Cl_2, $CHCl_3$, chlorobenzene), protic (e.g., MeOH, EtOH), nitriles (e.g., MeCN, PhCN). The test is ineffective with these solvents.

Cleanup:
- Follow the quenching and disposal procedure in the Pyrophoric Chemical SOP for materials that have come into contact with the Na metal.

Related SOPs:
- Pyrophoric chemical SOP
- Waste SOP

Appendix 1
Original Benzophenone Ketyl Radical Recipe
(Courtesy: Prof. Theo Agapie, Caltech)
In the glovebox, weigh 28 mg (1.22 mmol, 1.6 equiv) sodium metal into a 20 mL scintillation vial. Add 0.137 g (0.752 mmol) benzophenone (Ph_2CO), 20 mL THF, and a magnetic stir bar. Stir vigorously overnight. The clear, colorless solution should darken steadily to a blue color before eventually turning inky purple. The excess sodium will keep the indicating solution active and accurate for longer.

Derivation:
We want to test for < 10 ppm water in our solvents. What concentration of ketyl radical do we need?

For any solvent, we can choose the following parameters:
Desired maximum level of water impurity: $p \times 10^{-6}$ (p ppm)
$d_{solvent}$ = density of solvent to be tested
$FW_{solvent}$ = formula weight of solvent to be tested
FW_{Ph2CO} = 182 g mol^{-1} = formula weight of benzophenone indicator
Volume of solvent to be tested: V mL (normally 4 mL – full small vial)

Moles of solvent = $(V \times d_{solvent}) / FW_{solvent}$
- ⇨ Max moles of water = $(p \times V \times d_{solvent}) / FW_{solvent}$

Prepare 20 mL solution of indicator to have the appropriate concentration to discolor when one drop is added to *V* mL of a solvent containing more than *p* ppm water.

Mass of Ph_2CO in a drop of solution: $(p \times V \times d_{solvent} \times FW_{Ph2CO}) / FW_{solvent}$
Volume of one drop (disposable Pasteur pipet) ~ 0.013 mL (153 drops for 2 mL of THF)

Mass of Ph_2CO for 20 mL indicator solution:
$(p \times V \times d_{solvent} \times FW_{Ph2CO} \times 153 \times 10) / FW_{solvent}$

For testing THF:
- $FW_{solvent}$ = 72 g mol^{-1}
- $d_{solvent}$ = 0.889 g mL^{-1}
- V = 4 mL
- $p = 10 \times 10^{-6}$ = 10 ppm

Hence, $10\times10^{-6} \times 4 \times 0.889 \times 182 \times 153 \times 10 / 72 = 0.137$ g Ph_2CO for 20 mL indicator solution. Excess sodium was used (28 mg, 1.6 equiv).

Concentration of Ph_2CO in solution is 0.0377 M (moles L^{-1}).
For a different solvent, if the solution stays purple, max content of water is:
$p' = C_{Ph2CO} \times 0.000013 \times FW_{solvent} / (V \times d_{solvent})$

For pentane:
$FW_{solvent}$ = 72 g mol^{-1}
$D_{solvent}$ = 0.63 g mL^{-1}

V = 4 mL

⇨ p' = 14 ppm

Given that the solution prepared above precipitates a little solid, the concentration of ketyl radical is slightly lower, so the concentration of water in the solvent is even smaller. If even more rigorously dry solvents are required, the volume of solvent tested could be doubled.