Green Chemistry

edited by
Mary M. Kirchhoff
ACS Education Division
Washington, DC 20036

A Facile Solvent-Free Cannizzaro Reaction

An Instructional Model for Introductory Organic Chemistry Laboratory

Sonthi Phonchaiya and Bhinyo Panijpan
Institute for Innovation and Development of Learning Process, Mahidol University, Bangkok 10400, Thailand

Shuleewan Rajviroongit*
Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand; **scsrv@mahidol.ac.th*

Tony Wright
School of Education, University of Queensland, 4072, QLD, Australia

Joanne T. Blanchfield
School of Molecular and Microbial Sciences, University of Queensland, 4072, QLD, Australia

To make students in chemistry laboratory more appreciative of the environmental aspects of chemistry, it is important that the laboratory exercise address possible environmental impacts, for example, energy used, chemical wastes produced, and the use of organic solvents. A reaction that involves only a small amount(s) of reactants in an aqueous solvent with no organic solvent used in the product purification step would result in a greener chemistry laboratory. A pedagogical method such as guided inquiry will make the laboratory more learner-centered and should make the students more responsive to issues related to chemical pollutants *(1)*.

Currently there is a greater emphasis on chemistry laboratories that are environmentally friendly. An example is a recent article in this *Journal* illustrating a green Cannizzaro reaction without the use of solvent *(2)*. Here we offer another green Cannizzaro reaction laboratory that uses water for extraction and involves no heating of the reaction mixture.

We tried this laboratory with undergraduates in two universities. The students can follow the Cannizzaro reaction visually and then separate the products easily and cleanly. This reaction demonstrates disproportionation and oxidation–reduction as well as hydride transfer—a process important in many biological reactions *(3)*. In the guided-inquiry laboratory, students were required to design parts of the experiment and tackle problems relating to the reaction, as well as some extra problems on thermochemistry and green chemistry. These activities demanded more from the students compared with conventional laboratory experiments and should make their learning more profound and provide them with a broader perspective *(4)*.

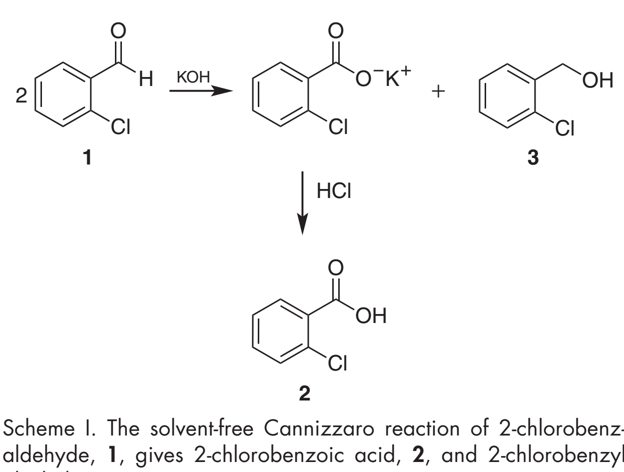
Chemistry

Liquid 2-chlorobenzaldehyde (17.8 mmol, 2.00 mL) and potassium hydroxide pellets (26.7 mmol, 1.50 g) were ground together in a pestle and mortar. Completion of the reaction, which usually takes around 30 minutes, was monitored by thin-layer chromatography (TLC). Reaction progress is also readily judged by appearance; that is, the gummy mixture of reactants turns into a thick paste. Students then take advantage of water solubility to separate potassium 2-chlorobenzoate from 2-chlorobenzyl alcohol by filtration: the solid 2-chlorobenzyl alcohol retained by the filter was washed twice with water. After acidification of potassium 2-chlorobenzoate and filtration, the precipitated 2-chlorobenzoic acid was also rinsed with water. In both cases small amounts of products were sacrificed, leading to slightly reduced yields. The reaction is shown in Scheme I.

Students achieved yields of 35–85% for each pure product. They characterized their partially dried products by comparing the R_f values on TLC with the authentic samples. The IR and NMR spectra of the products (dried in the desiccator) were as pure as authentic samples. A mixed melting point determination is also a useful option where appropriate.

Hazards

2-Chlorobenzaldehyde, 2-chlorobenzoic acid, and 2-chlorobenzyl alcohol are skin, eye, and respiratory irritants and may be harmful if swallowed. Hexane and ethyl acetate are highly flammable and volatile. Inhaling hexane and ethyl acetate may cause drowsiness and can damage health. Potassium hydroxide is caustic and can cause severe burns. Hydrochloric acid is corrosive and may cause damage to skin.



Scheme I. The solvent-free Cannizzaro reaction of 2-chlorobenzaldehyde, **1**, gives 2-chlorobenzoic acid, **2**, and 2-chlorobenzyl alcohol, **3**.

Pedagogic Approach

Students were assigned to read the instructions and asked to hand in a pre-lab exercise before beginning the experiment. This exercise introduced the students to the chemical hazards of substances to be used, the oxidation state of the functional groups, and the chemical equation of the redox reaction.

The laboratory instructions are divided into four parts. Part 1 outlines the procedure for carrying out the reaction in the mortar as well as the instructions for TLC monitoring so that students can check the reaction progress and then continue to the separation step when the reaction is complete. Part 2 provides necessary information for students to design the procedure for separation and identification of their products. The solubility properties of 2-chlorobenzyl alcohol, potassium 2-chlorobenzoate, and 2-chlorobenzoic acid and the instructions for vacuum filtration and acidification are provided. Authentic samples of the two products together with their melting points, IR, and ^{1}H NMR spectra are provided. Part 3 provides guidelines and resources to explore the energies of the reaction and answer the question why the reaction should occur. The molecular modelling software (Spartan 06 programme) and the thermodynamic data from *NIST Chemistry WebBook (5)* are useful. Part 4 introduces students to the basic concepts of green chemistry and outlines a strategy to compare this experimental procedure with a traditional Cannizzaro reaction based on the 12 principles of green chemistry. The 12 principles of green chemistry *(6)* are provided.

Guided Inquiry

To introduce an element of inquiry, this experiment has been developed using some "adaptation principles" *(7).* These change the purpose statement of the activity into a *question*, giving students opportunities in a simple way to develop procedures and make predictions. The format engages them in the analysis and explanation of data.

Three aspects of the experiment—separation, characterization, and thermodynamics—have been adapted for (guided) inquiry. First, students are given the responsibility to design their own procedure for the separation and characterization as indicated in Part 2. As a consequence, their understanding of physical properties, solubility, and adsorption characteristics that bear on the R_f values on TLC, absorption bands in the IR, as well as ^{1}H NMR spectroscopy, will be reinforced.

Next, student attention can be drawn to one of the interesting questions about the Cannizzaro reaction: Why does the reaction occur? Answering this question can lead to an exploration of the thermodynamics of the reaction. Students can interpret enthalpy data in terms of whether the reaction is exothermic or, if they have covered the second law of thermodynamics, they can compute the Gibbs energy to determine whether the reaction is likely to occur spontaneously. Further information on our guided inquiry is included in the online materials.

Our preliminary data from questionnaires and interviews indicate that most students taking this laboratory preferred such a learner-centered exercise to a conventional one and that they acquire a better understanding of the chemistry and of chemical industry-related environmental issues. Therefore, we recommend this laboratory for first- or second-year undergraduate students, especially those who have been exposed to functional group organic chemistry, general chemistry, and some experimental methods in chemistry.

Green Chemistry

This experiment is an ideal example of the application of green chemistry principles. In the experiment, students use the 12 principles of green chemistry as an analytical tool. Broadly, students are required to think about the less harmful solvents used in the reaction, the minimum use of energy, as well as minimizing waste generation. They should be able to compare their procedures with conventional ones in terms of environmental impact, economics, and human health hazards. Some of the principles may require information that is not readily available, such as biodegradability and some hazard information. This presents students with an opportunity to use the chemical literature before making a decision.

Acknowledgments

We would like to thank The Institute for the Promotion of Teaching Science and Technology (IPST), Thailand, for a grant that made it possible for this collaboration between Mahidol University, Thailand, and the University of Queensland, Australia. We thank E. J. Wood for reading the manuscript.

Literature Cited

1. Marteel-Parrish, A. E. *J. Chem. Educ.* **2007,** *84,* 245–247.
2. Esteb, J. J.; Gligorich, K. M.; O'Reilly, S. A.; Richter, J. M. *J. Chem. Educ.* **2004,** *81,* 1794–1795.
3. McMurry, J. *Organic Chemistry: A Biology Approach;* Thomson Brooks/Cole: Canada, 2007; pp 579–580.
4. Barrow, L. H. *J. Sci. Teacher Educ.* **2006,** *17,* 265–278.
5. *NIST Chemistry WebBook;* National Institute of Standards and Technology (NIST); *http://webbook.nist.gov/chemistry* (accessed Oct 2008).
6. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice;* Oxford University Press: New York, 1998.
7. Volkmann, M. J.; Abell, S. K. *The Science Teacher* **2003,** *70,* 38–41.

Supporting *JCE Online* Material

http://www.jce.divched.org/Journal/Issues/2009/Jan/abs85.html

Abstract and keywords

Full text (PDF)

Links to cited URLs and *JCE* articles

Supplement

Handouts for the students including pre-lab questions and post-lab exercises

Notes for the instructor

Spectroscopic data