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## The Pyrolysis of Polystyrene

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**Abstract:** An experiment suitable for the first semester of a two-semester organic chemistry laboratory sequence is described. This experiment is carried out in the problem-solving mode. Students are instructed to pyrolyze polystyrene and to gather sufficient data for the unequivocal identification of their pyrolysis product.

### Introduction

An experiment we have used for several years in our undergraduate organic chemistry laboratory is the pyrolysis of polystyrene. On pyrolysis, depolymerization of the polystyrene occurs and the product is styrene. This experiment introduces a new concept for most of our students, who generally consider polymers to be unreactive species only undergoing complete destruction upon intense heating. The experiment is the reverse of the polymerization of styrene that has been reported in the literature [1–3] and appears in many laboratory texts. It is unique in that the degradation of a compound is studied rather than its synthesis.

We have debated whether to call this a thermolysis or pyrolysis reaction. *Pyro* is from the Greek root meaning fire, while *thermo* means heat. *Lysis* means loosening or dissolution. It seems that thermolysis is probably the more correct term, but in the United States pyrolysis has been used to describe this kind of reaction [4, 5].

### Pedagogy

We use this experiment in the problem-solving mode described previously [6]. The problem to be solved, a common one for a chemist running an organic reaction, is to determine what happened under their experimental conditions. Did a straightforward reaction occur and what evidence is needed to identify the product(s)? Students are instructed to heat polystyrene using a simple distillation apparatus until a product distills and to collect the distillate. They are then asked to speculate on what reaction took place and to identify the product. The organic chemistry laboratory, like the science laboratory in general, exists as a place to make observations and gather data. To mimic real-world laboratory experiences, students should also be asked to perform these tasks. The data collected should then be *used* to gain insight into the problem under investigation (in this case, to identify an unknown product) thereby simulating what a scientist does. The laboratory ought to teach how the information that is communicated so quickly in the lecture part of the course and makes up the body of the subject of organic chemistry has been obtained. An advantage of a problem-solving approach is that students do more careful work when they are getting data to be used for interpretation, and we feel they learn standard laboratory techniques as well or better than in a more traditional course.

For us, the most important aspects of this experiment are that the student uses good technique to obtain the product and determines an adequate amount of data to be able to make a convincing case for identification. We expect the student to communicate the description of the data in the form of a report consisting of an interpretation of the data that leads to a conclusion, and comparison of the data with that reported in the literature. The style of the report should resemble original research papers in chemical journals. A major aim and emphasis is the understanding gained and displayed by the student.

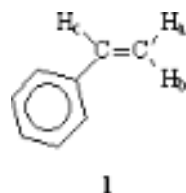
Currently the experiment is being used in the latter part of the first semester of the two-semester sequence of laboratory work in organic chemistry. The student's background from the lecture part of the course at this point includes some exposure to the thermal cracking of alkanes and an introduction to alkenes, but precedes a discussion of aromatic compounds. In the laboratory, methods for obtaining physical properties, distilling, running thin-layer chromatograms, and IR and NMR spectra have been introduced. Students have been instructed on the interpretation of IR and NMR spectra. Also emphasized is the usefulness of these methods for the accumulation of data to identify a compound. To compel the student into realizing what the importance of various types of data are, we ask students to decide for themselves what data to collect to identify the product. Most students conclude that they could probably identify their product from its NMR spectrum; however, they also decide that for a full characterization of their product a boiling point should be reported and an IR spectrum and determination of its refractive index are required. In addition, many students choose to run a thin-layer chromatogram to further evaluate the purity of their product and to help confirm its identity by comparison with an authentic sample of styrene. Consequently, this experiment serves as a review of most of the semester's work.

### Data for Product Identification

The product is a colorless mobile liquid, bp 141–142 °C at 690 mm. Our elevation is 2500 feet above sea level and using a correction of 0.5 °C per 10 mm gives a corrected bp of 144.5–145.5 °C at 760 mm (lit [7], 145.2 °C). The product migrates as a single spot on the thin-layer chromatogram with a  $r_f$  of 0.57 (silica gel and hexane). From this observation the student is expected to conclude that the product is probably a pure compound and that it is relatively nonpolar. The refractive index is 1.5465 (lit [7], 1.5468). Students are expected to determine IR and NMR spectra on their own samples. IR spectrometers are available for student use in our teaching laboratories. In our program, the student prepares a sample for NMR, but a technician records the spectrum and makes the free-induction-decay (FID) signal available electronically to the student. The student Fourier transforms their FID and obtains the NMR spectrum of his or her sample. We expect our students to expand critical regions of their spectrum to allow the accurate determination of coupling constants and to include a full interpretation of their spectral data in their laboratory reports. For the majority of our students, this is their first encounter with a “complex” splitting pattern and it serves as an extremely valuable lesson in the interpretation of more difficult NMR spectra.

The alkene group and the monosubstituted benzene ring can be identified using the IR spectrum. Peaks at 1630 and also 910 and 990  $\text{cm}^{-1}$  are reported, and the expected interpretation is that they are due to C=C stretching displaced to lower frequency by conjugation and,  $-\text{CH}=\text{CH}_2$  out-of-plane bending, respectively. Peaks at 1660 to 2000  $\text{cm}^{-1}$  and also at 698 and 750  $\text{cm}^{-1}$  provide an identification of the monosubstituted benzene. Finally, four peaks in the region 3000 to 3080  $\text{cm}^{-1}$  indicate Ar–H and  $=\text{C}-\text{H}$  stretching. This level of detail meets our expectations for an acceptable interpretation. The best reports also contain a reference to a published IR spectrum of styrene [8].

The product identity usually is confirmed using proton NMR, and the interpretation of the  $^1\text{H}$  NMR spectrum is excellent experience for the beginning student. Observed data with the expected interpretation, for styrene (**1**), are as follows:  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , d,) for the vinyl group  $\text{H}_a$  5.55 (1H, dd,  $J = 10.9$  Hz,  $J = 0.9$  Hz),  $\text{H}_b$  5.72 (1H, dd  $J = 17.6$  Hz,  $J = 0.9$  Hz),  $\text{H}_c$  7.01 (1H, dd,  $J = 10.9$  Hz,  $J = 17.6$  Hz) and for the phenyl ring 7.7 (5H, m). An explanation of splitting as well as a comparison with the published spectrum [9] is expected. The small coupling of  $\text{H}_a$  and  $\text{H}_b$  may be missed in low-resolution spectra.



For programs where spectroscopy is not available, the instructor could provide the students with the spectra, which we have included as supporting material with this article. Alternatively, the product could be identified using classical methods of qualitative organic analysis [10]. We do not formally introduce qualitative analysis in our laboratories until the second semester of the two-semester sequence. To make qualitative analysis more accessible to our students and also feasible to be carried out in a limited number of three-hour laboratory periods, we have adapted [10] the systematic approach to qualitative analysis of Shriner and Fuson [11]. An introduction to solubility, classification tests, and derivative formation for the classes of compounds (alkanes, alkenes, alkyl halides, alcohols, and ethers) can be accomplished in three three-hour laboratory periods. We use materials we have developed for such purposes in our program [12]. These functional groups are usually covered during the first semester of a yearlong course in organic chemistry, and qualitative analysis serves to illustrate the many reactions of these functional groups discussed in the lectures. Styrene is a typical unknown to use in qualitative analysis.

The product obtained upon pyrolysis of polystyrene is insoluble in water and soluble in concentrated sulfuric acid showing it to be either an oxygen-containing compound or an alkene. It gives alkene tests—decolorizing bromine and permanganate solutions, and it readily forms a solid dibromo derivative. Similarly, it is easily oxidized to benzoic acid. Tables [13] listing classes of compounds, such as alkenes, in order of increasing boiling points and melting points are particularly helpful in the identification of compounds classified using a qualitative-analysis scheme. These same tables list the melting points of appropriate derivatives.

We use a flexible evaluation scheme. Students receive credit for correctly interpreting the data they report and, in particular, on how well they demonstrate their understanding in writing their reports. After the student reports have been graded, we recommend a follow-up session in which students present their data and the instructor assists in giving the correct interpretation. Students comment favorably on these sessions and find them very helpful in understanding the experiment and in providing direction for subsequent experiments.

## Experimental Section

**Hazards.** The product of this reaction has a strong odor, is flammable, and is moderately toxic [14]. Avoid contact with the skin and avoid breathing the vapors. It is desirable to carry out the pyrolysis in the hood, but many undergraduate laboratories have inadequate hood space. In such cases, instructors need to check to see that each distillation apparatus is correctly assembled with ample provision for complete condensation of the product. The product should also be transferred and handled in the hood if possible.

**Procedure.** Place 2 g of polystyrene in a 25-mL round-bottom flask. Styrofoam cups are readily available and work well as the source of polystyrene for this experiment. The Styrofoam “peanuts” loose packing material is of too low a density to be useful in this experiment. Set up a simple distillation apparatus. It is not essential to use a water condenser with this distillation. The receiver may be cooled with an ice-water bath, and is recommended if there is inadequate hood space for the pyrolysis. To bring about pyrolysis and obtain a distillate from this sample, it is necessary to heat the sample strongly [15]. Either a heating mantle or a flame (*extreme caution should be exercised if a flame is used due to the flammability of styrene*) at least two-inches high directly on a wire gauze will suffice for the pyrolysis. Distill about one milliliter of product. Use the methods you have already learned to decide if the product is pure and to identify it. The still pot may be cleaned with a few mL of toluene [16].

**Supporting Materials.** IR and NMR spectra of styrene are available in a Zip file. (<http://dx.doi.org/10.1333/s00897030720a>)

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14. Emergency overview from the Fisher Scientific Materials Safety Data Sheet ([www.fishersci.com](http://www.fishersci.com)): Appearance: clear colorless to light yellow liquid. Flash Point: 32 deg C. **Warning! Flammable liquid and vapor.** Aspiration hazard if swallowed. Can enter lungs and cause damage. May cause eye and skin irritation. May cause respiratory and digestive tract irritation. May cause central nervous system depression. Light sensitive. Air sensitive. May cause cancer based on animal studies. Uninhibited material, or material from which the inhibitor has been removed or reacted, may form explosive peroxides. **Target Organs:** Central nervous system.
15. Pyrolysis commences at a mantle temperature of about 290 °C, but higher temperatures are required for efficient distillation in macroscale glassware.
16. The still pot is difficult to clean but on soaking with a few mL of toluene the residual polystyrene will come away from the glass. Some black residue is formed and can be scrubbed out with soap and water. Because the flask is difficult to clean some instructors set aside enough flasks for this specific experiment. Continuing the thermolysis until the polystyrene is gone and then scrubbing the residual carbon out with soap and water may achieve cleaning. Because, as a general practice, it is dangerous to continue a distillation to dryness, we do not instruct students to clean their flasks in this way.