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Demonstration

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Demonstration of Thermodynamics and Kinetics Using FriXion Erasable Pens

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Ⓢ *Supporting Information*

ABSTRACT: FriXion erasable pens contain thermochromic inks that have colored low-temperature forms and colorless high-temperature forms. Liquid nitrogen can be used to kinetically trap the high-temperature forms of the ink at temperatures at which ordinarily the low-temperature forms are more thermodynamically stable.

KEYWORDS: *First-Year Undergraduate/General, General Public, Demonstrations, Public Understanding/Outreach, Hands-On Learning/Manipulatives, Acids/Bases, Consumer Chemistry, Kinetics, Thermodynamics*

FEATURE: Tested Demonstration

In 2006, Pilot Pens, Inc. released the FriXion erasable ball pen, a new type of erasable pen.[1] Previous erasable pens, such as Papermate's Erasermate, erased ink by using a conventional rubber eraser that physically lifted ink and some paper away from paper surfaces.[1,2] The ink from the FriXion pens is "erased" by a completely different phenomenon; the heat caused by friction between its hard, smooth plastic "eraser" and the paper containing the ink causes the thermochromic ink to turn colorless. This color change has also been found to be reversible.[3] Naturally, this phenomenon has sparked questions regarding the reactions taking place during the color changes, including the nature of the reactants and products and the temperatures at which these reactions take place.

The temperatures at which these reactions occur can be gleaned from the warnings issued by the manufacturer:[3]

> Do not expose to extreme temperatures (<14 °F; >140 °F) [< −10 °C; >60 °C]. If pen is exposed to temperature that reaches 140 °F [60 °C], the ink will be colorless when writing. To restore color, cool to at least 14 °F [−10 °C] in freezer and the ink will again write in color.

Therefore, the color change is not a simple reversible process characterized by a single transition temperature; rather, the transition from colored (low-temperature) to colorless (high-temperature) ink occurs at a much higher temperature (∼60 °C) than the reverse transition (∼ −10 °C).

Finding the specific nature of the species involved in the reactions was problematic. Representatives from Pilot Pens, Inc. were not forthcoming with detailed information, suggesting instead an exploration of the patent literature. U.S. patents describe thermochromic systems with at least three components:[4−8]

(1) one or more compounds such as various spiropyrans and triarylmethane dyes such as fluorans to act as "electron donors" (bases) and reversibly change color upon reaction with acids,
(2) one or more compounds such as various phenols or 1,2,3-triazoles to act as weak acids to produce the color change in the first component
(3) one or more compounds to regulate the temperatures at which the color transitions take place, for example, esters or alcohols. Above these transition temperatures, the reaction causes loss of color (eq 1, forward direction). Below these color transition temperatures, the electron donors (bases) are protonated and show color (eq 1, reverse direction).

$$\text{Dye-OH (colored)} + \text{A:-} \rightleftharpoons \text{Dye-O:- (colorless)} + \text{HA} \quad (1)$$

Thermochromic color technology related to these patents was used in the Hypercolor brand of clothing.[6,9] These clothes used triarylmethane dyes, triazoles, and an alcohol solvent that also contained an ammonium salt of a fatty acid. At relatively low temperatures, the salt remained associated and the triazole caused the dye (crystal violet) to be in the colored form. At relatively high temperatures, the alcohol solvent melted and the

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salt dissociated, allowing it to neutralize the triazole, which in turn converted the dye to the colorless form.

■ PROPERTIES OF THE THERMOCHROMIC INKS

The acid–base sensitivity of the FriXion ink colors have been explored. Addition of 3 M HCl or 3 M H_2SO_4 to six colors of dry FriXion ink in the low-temperature, colored form spread on paper caused them to at least partially keep their color at elevated temperatures (when normally these inks would turn colorless). Addition of these acids to these same dry ink colors *after* conversion to the high-temperature, colorless form caused them to revert to their colored form.[10] However, addition of 3 M NaOH or 3 M NaCl had little or no effect on whether the ink streaks on paper kept their color at high temperatures and regained their color at low temperatures. Wet black FriXion pen ink extracted from the pen body was more responsive to pH changes: combination of the ink with either 98% or 6 M H_2SO_4 acid kept the ink colored,[11] but when base (e.g., 50% NaOH) was added, the mixture turned colorless. The color could be restored by additional H_2SO_4.[12]

Examination of the inks by optical microscopy revealed that they have a granular structure, most likely due to micro-encapsulation of the ink. Many of the granules are in the 1–2 μm size range, with relatively few up to about 8 μm in size. The physical structures of these granules do not appear to be visibly damaged by most aqueous solutions, but some acids and bases do appear to be able to penetrate the granules, affecting the ability of the ink to change color. These acid and base experiments are consistent with the reactions described in the patent literature and support the model that the dyes in the inks are not only thermochromic, but also affected by pH and are therefore halochromic.

The thermochromic properties of these FriXion inks enable them to be used to illustrate the roles of thermodynamics and kinetics in chemical reactions. With sufficient time, the ink components will reach their thermodynamically favored colored forms at low temperatures and their thermodynamically favored colorless forms at high temperatures, Figure 1.

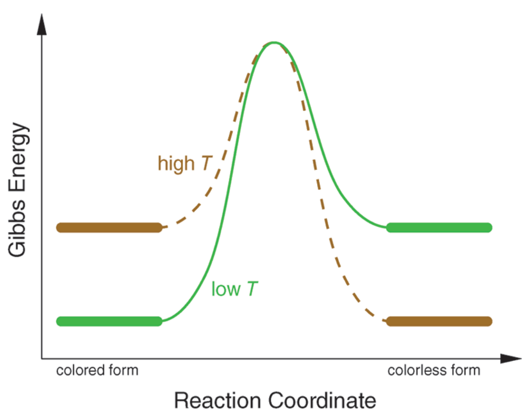

Figure 1. Free energy diagrams for the thermochromic ink at low and high temperatures, depicting the activation barriers for the conversion between the colored and colorless forms.

Differential scanning calorimetry (DSC) on a sample of black FriXion ink revealed that, as it was heated, its dominant endothermic transition was about 57–60 °C (with no exothermic transition in that range), and as the ink was cooled, its dominant exothermic transition was about −3 to 0 °C (with no endothermic transition in that range). Overall, these temperature ranges were consistent for wet ink, dry ink, or ink with aqueous HCl, NH_3, or NaOH added and are also consistent with the temperatures mentioned in the description from the manufacturer cited above.[3]

The activation barrier for interconversion of both forms of the ink components is sufficiently high that both forms can exist for very long times at room temperature. This is a sort of color hysteresis—the ink form that exists at room temperature depends on the direction from which room temperature is reached.[7] A schematic color hysteresis curve for the thermochromic ink is shown in Figure 2. Beginning with colored ink at point A below the color transition temperature, as the ink is heated (e.g., by rubbing with the pen eraser), it traverses the upper pathway, attaining a relatively high temperature (~60 °C) before the color changes and eventually ends up at point B. When the ink is slowly cooled from point B, it traverses the lower pathway, attaining a relatively low temperature (~0 °C) before the color changes and eventually ends up at point A. If the high-temperature (colorless) form of the ink is cooled very rapidly to very low temperatures with liquid nitrogen, the ink remains kinetically trapped in the colorless state, changing the cooling pathway shown in Figure 2. However, the ink converts from colorless to colored as it is warmed back up from these low temperatures. These phenomena can be demonstrated to a classroom.

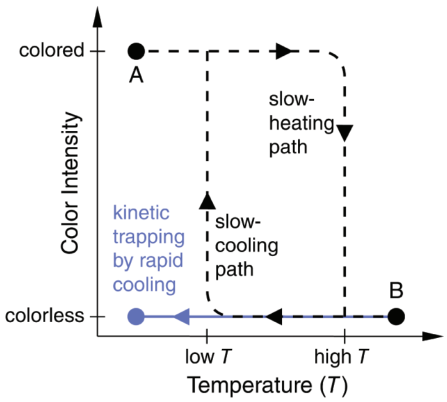

Figure 2. Schematic color hysteresis curve for the thermochromic ink, including the kinetic trapping of the colorless form of the ink.

■ MATERIALS

- FriXion erasable pens or highlighters (Pilot Corporation of America, Jacksonville, FL)
- thin, light-colored paper, such as standard white printer paper
- blow dryer or heat gun
- wide mouth Dewar flask (about 1 L capacity)
- liquid nitrogen
- tongs or long forceps
- goggles, heavy leather gloves, lab coat for protection from liquid nitrogen

■ HAZARDS

Standard procedures for use of liquid nitrogen should be used in this procedure. Gloves, lab coats, and goggles will reduce the chance of liquid nitrogen affecting one's skin and eyes. Dewar flasks used to contain liquid nitrogen have an ever-present implosion hazard and should be handled carefully.

DEMONSTRATION

Write on a light-colored piece of paper with the FriXion erasable pen or highlighter (darker ink colors are more visible). Show the ink marks to the audience. Roll the paper into a tube shape and quickly dip it into the Dewar flask of liquid nitrogen. Gloves and tongs are recommended. After at least 5 s, quickly remove the paper from the liquid nitrogen and show the paper to the audience to reveal that liquid nitrogen does NOT cause the ink to turn colorless. Use the blow dryer or heat gun to show how the ink "disappears" at high temperatures. If desired, the ink can be potentially recolored by cooling it, but NOT by cooling it in the liquid nitrogen. When the ink is colorless, again roll the paper into a tube shape and quickly dip it into the Dewar flask of liquid nitrogen. Again, gloves and tongs are recommended. After at least 5 s, quickly remove the paper from the liquid nitrogen and show the paper to the audience. For a brief time, the ink remains colorless and kinetically trapped in the high temperature state. Sometimes, some of the ink (e.g., the pink highlighter ink) partially converts to the colored form, taking on a sort of faded appearance. As the ink and paper warm to room temperature (but are still cold relative to the transition temperatures), the colorless, high-temperature form of the ink converts to the colored, low-temperature form. Wiping a hand across the cool paper will help speed up the re-emergence of the color (and adds a little more drama to the demonstration).

DISCUSSION

To keep the FriXion erasable ink colorless at low temperatures, it must be cooled so quickly that it does not have sufficient energy to surmount any kinetic activation barriers, preventing the ink from converting from the thermodynamically most stable high-temperature colorless form to the thermodynamically most stable low-temperature colored form, Figures 1 and 2. This is an example of kinetic trapping, which manifests itself in other ways in chemistry. For example, in metallurgy, metals that are cooled rapidly often trap thermodynamically unstable atomic patterns before they can rearrange to more stable patterns.[13] Similarly, in "self-assembled" systems, metastable structures can form rather than more thermodynamically stable arrangements unless some energy is used to redisperse these structures.[14] Intermediates in biochemically catalyzed reactions can be trapped at liquid nitrogen temperatures and characterized by X-ray diffraction before they are converted to more thermodynamically favored species.[15]

Unsuccessful attempts have also been made to use liquid nitrogen to trap high-temperature colors of color-changing materials such as a liquid crystal sheet (by immersing the sheet in the liquid nitrogen) and a thermochromic plastic cup (by pouring the liquid nitrogen into the cup). It is likely that these materials, which are thicker than a film of ink on a sheet of copier paper, have a greater heat capacity and therefore cool too slowly to trap the high-temperature color. This explanation is supported by a similar experiment in which marks of the colorless (high-temperature) form of the ink on cardboard partially re-colored in contact with liquid nitrogen, whereas on thin paper, they remained kinetically trapped in the colorless state. This FriXion ink demonstration vividly illustrates how low temperatures and slow reaction kinetics enable the trapping of thermodynamically unstable forms of matter.

ASSOCIATED CONTENT

Supporting Information

A movie of this demonstration (avi file). This material is available via the Internet at http://pubs.acs.org.

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Notes

Thomas P. Gonnella (Department of Chemistry, Mayville State University, Mayville, ND 58257) tested this demonstration.

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(10) The acids were added to the ink drawn on light-brown paper towels. Acids fizzed when added to white copy paper, presumably because the acid was being neutralized by calcium carbonate present in the paper.
(11) When 98% H_2SO_4 is combined with wet black FriXion pen ink, the ink color shifted to orange. Addition of water, even from humidity in the air, changed the color back to black.
(12) Combining high concentrations of acid and base, even in small quantities, can produce violent chemical reactions, so caution is advised.
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