THE CHEMISTRY OF AUTOCATALYTIC PROCESSES IN THE CONTEXT OF THE SHROUD OF TURIN

Raymond N. Rogers
Fellow
University of California, Los Alamos National Laboratory
rnrogers@att.net
17 October 2002

Abstract

Based on the facts of chemistry and current storage conditions, the Shroud of Turin is in no danger of autocatalytic decomposition.

Autocatalytic chemical reactions are those in which the rate increases as the materials react. The most important single factor in predicting effects is the ***temperature***. When the temperature changes, the rate changes. The only severe heating episode the Shroud has suffered was during the fire of 1532. Any autocatalytic decomposition that occurred then has long since stopped as the Shroud is stored at normal temperatures.
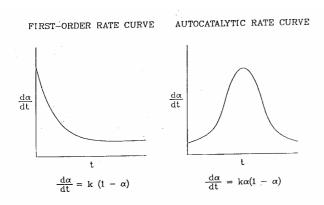
Autocatalysis can not rigorously be discussed without some reference to basic chemical kinetics and mathematics. The fundamental equation that describes an autocatalytic process is the following:

$$\frac{d\alpha}{dt} = k\alpha^{p}\left(1-\alpha\right)^{q}Ze^{-\frac{E}{RT}}$$

where α is the fraction reacted at any specific time, t. The derivative, $d\alpha/dt$, is the rate of the reaction. E is the "Arrhenius activation energy," and Z is the "Arrhenius pre-exponential." Each applies ***only*** to a single specific, consistent reaction being studied. The value of the "rate constant," k is different at each specific temperature: It is a *constant* only at one temperature, and it applies ***only*** to one specific reaction. The values of E and Z are determined from a large number of k measurements at different temperatures. Predictions of the Shroud's expected lifetime can not be made on the basis of a single rate constant. Observations made during a scorching event can not be applied to rates at normal temperatures.

E, Z, and k are the most important values in a discussion of rates and associated lifetimes of materials. All of these values have fundamental meaning in the chemical reaction. R is the "gas constant (1.9872)," a universal constant that applies to many disparate physical and chemical processes, and it is known with great accuracy and precision. T is the *absolute* temperature, expressed in degrees Kelvin (0K = -273.2°C). The exponents p and q allow the prediction of the position of the maximum rate in an autocatalytic process, i.e., the amount reacted at the maximum rate - ***at constant temperature***. Exponents higher than 2 are extremely rare.

Examples of simple and autocatalytic rate curves are shown in the figure. Notice that the rate increases with time in the autocatalytic curve, **at constant temperature**, until it reaches a maximum reaction rate.   Then the rate decreases.   However, **the initial rate at any temperature is much lower than the maximum rate.** The decomposition rate of cellulose is essentially zero at room temperature. When cellulose is decomposing at high temperature, the rate can be returned to its initial value by cooling.

FIRST-ORDER RATE CURVE   AUTOCATALYTIC RATE CURVE

$$\frac{d\alpha}{dt} = k\,(1 - \alpha)$$ $$\frac{d\alpha}{dt} = k\alpha(1 - \alpha)$$

The activation energy, E, is closely related to the strength of the reacting chemical bond. Strong bonds show high activation energies when they react, weaker bonds show lower activation energies.   The bond that breaks at the highest rate in the initial pyrolysis of cellulose is the C-OH bond on the hydroxymethyl functional group. That bond has an energy on the order of 80 kcal/mole. It is not a weak bond.

Activation energies in solids, *especially crystalline solids like cellulose,* are higher than the values for the same material in a solution or melt, because a crystalline lattice is stabilized by its ordered structure. Cellulose is composed of very long polymer chains of sugar molecules. The chains are folded back and forth in a regular pattern that shows the properties of crystallinity, which is called a "fibrillar structure" in materials like linen.   Some zones between the small crystals are amorphous, and they act more like cellulose would in a melt. The amorphous zones would decompose more readily than the crystalline zones; however, the rate constants for such decomposition predict extremely slow decomposition, so slow you can call it zero.

The major cause for autocatalysis in cellulose decomposition is the destruction of crystalline order when the material is heated to a high temperature. Secondary, chemical autocatalysis is discussed below. Rates in the normal cellulose solid phase are essentially zero in the absence of short-wavelength light.

When crystalline order is destroyed by heating, autocatalysis involves a process like "melting with decomposition." Rates are much higher in a melt than in the solid; therefore, melting increases decomposition rates.   When the material is cooled below the melting point, autocatalysis stops entirely. The difference between E in a melt and in the crystalline solid is often close to the latent heat of fusion. *Melted materials decompose more rapidly than the*

same material in a solid phase [Rogers, R. N., "Differential Scanning Calorimetric Determination of Kinetics Constants of Systems that Melt with Decomposition," Thermochimica Acta <u>3</u>, 437 (1972)].

The decomposition rate of a crystalline solid depends on crystal perfection. When crystals are put under stress, they develop high-free-energy defects, and decomposition is much faster at the defects than it is in the parent material. If autocatalysis were a real problem for the Shroud, significant differences should have been observed in damage around the stressed and strained stitching of the patches. There is no sign of accelerated autocatalysis, indeed there is no sign of any autocatalysis. Autocatalysis is not a real hazard for the Shroud.

Some reactions involve *chemical* autocatalytic rate processes in which a product (or products) of the primary reaction is a catalyst for the reaction: The rate increases as catalytic products accumulate **at constant temperature.** Small changes in the composition of the reacting material can have very large effects on the values of E and Z, as in any case of catalysis. If the process is cooled, the rate will be much lower, depending on the magnitude of E and retention of the catalytic product(s).

If catalytic products are gases, they can escape from the reacting zone after cooling. The autocatalytic process stops until another heating episode. There is no "memory effect." The primary chemical catalyst in the decomposition of cellulose is steam; therefore, cellulose does not show any measurable memory effect. The Shroud should be as stable at room temperature as any other sample of linen.

The primary decomposition process of all carbohydrates, including cellulose (linen), is dehydration, the loss of water. However, linen adsorbs and absorbs water from the atmosphere, depending on the relative humidity and temperature. When linen is heated, water immediately begins to be desorbed, the linen dries out. This can have a major effect on measurements of the weights of large pieces of cloth. It is somewhat difficult to determine the difference between adsorbed water and water of reaction when linen is heated. It may require measurements involving kinetic isotope effects with deuterium.

The structure of pure, uncatalyzed, crystalline cellulose (linen) does not begin to dehydrate at a significant rate until about 300°C [R. N. Rogers, *A Compilation of DTA and Pyrolysis Curves*, GMX-2-R-61-1, 1 March 1961, Published by the Los Alamos Scientific Laboratory, Los Alamos, NM, USA], and it is an extremely slow process at normal temperatures. Samples of wood and textiles exist from thousands of years ago; some of the oldest linen samples are in the superb Museum of Egyptology in Turin.

I could not observe any chemical autocatalysis in cellulose at normal temperatures. However, if Shroud deterioration is still a worry, the only practical way to slow the rate is to keep it cold, which also has the advantage of reducing microbiological attack. As in the case of the use of "inert" atmospheres, storage at reduced temperature should carefully be considered. Too cold a temperature could cause physical stress and might cause fibers to fracture. It would probably cause the thin coating of image color on the fibers to be loosened in some areas.

3

As a rule of thumb according to the Arrhenius expression, rates of normal reactions are increased by a factor between two and three for each 10 degrees increase in temperature. The effect is much larger when a phase change is involved, e.g., melting. Some moderate cooling could have a significant effect on prolonging the life of the Shroud. Severe freezing could damage the cloth.

The possibility for chemical autocatalysis in linen depends on the products of cellulose decomposition. Feigl and Anger [Feigl, F. and Anger, V., 1966, *Spot Tests in Organic Analysis,* Elsevier Pub. Co., New York.] describe the cellulose pyrolysis process as follows: "When cellulose is heated it decomposes and the resulting superheated steam reacts with unchanged cellulose to produce hexoses, which in turn hydrolyze to give hydroxymethylfurfural." The only important chemical catalyst for the autocatalytic degradation of cellulose at high temperatures is ***superheated steam***. Superheated steam does not exist at normal temperatures, and degradation of the Shroud can not be chemically autocatalytic as currently stored.
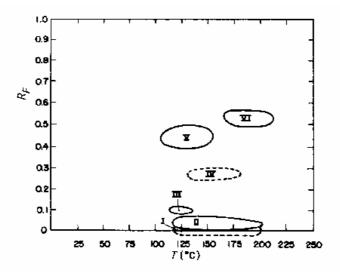
More detailed studies have shown that the condensable secondary products of the thermal decomposition of cellulose are furfural (2-furaldehyde), hydroxymethylfurfural (5-hydroxymethyl-2-furaldehyde), levulinic acid (4-oxopentanoic acid), and 3-pentenoic-γ-anhydride. None of these can be expected to be a significant catalyst for the autocatalytic decomposition of linen. I found that cellulose produced relatively more levulinic acid than furfural when compared with pentoses [Rogers, R. N., "The Chemistry of Pottery Smudging," Pottery Southwest 7, No. 2, 2 (1980)]. That is not a problem in the context of the Shroud. Levulinic acid is a solid at room temperature (mp 37.2C); it partially decomposes at its boiling point (245C), it decomposes much faster at higher temperatures and in oxygen, as during the fire of 1532; and it is an extremely weak organic acid that would have little effect on cellulose. It has a significant vapor pressure, and it gradually vaporizes from any surface.

I measured activation energies and decomposition mechanisms for the individual decomposition products of several carbohydrates [Rogers, R. N. and Smith, L. C., 1970, "Application of Combined Pyrolysis - TLC to the Study of Chemical Kinetics," J. Chromatog. **48**, 268]. One example, the rapid, ***catalyzed*** decomposition of the pure hexose sugar levulose, is shown in the figure. The sugar units in linen are glucose, a hexose.

I caught the products of decomposition on a thin-layer chromatographic plate as a function of the temperature at which the levulose was decomposing. I then "developed" the plate by allowing 1,2-dichloroethane to migrate up it from bottom to top. The more soluble and/or less strongly adsorbed products were pushed farther up the plate by the solvent. R_f is the ratio between the distance the single product migrated and the distance to the leading edge of the solvent. The distance the products migrated and chemical spot tests made it possible to identify them.

This reaction has been chosen to illustrate a ***catalyzed*** carbohydrate decomposition. It would be hard to find a more rapid decomposition of the kinds of molecules seen in cellulose (linen). It was catalyzed with concentrated phosphoric acid, a nonvolatile, strong, inorganic acid. The vertical axis shows the R_f (identity) of each specific product; the horizontal axis shows the

temperature at which the product appeared. II is levulinic acid, which decomposes to produce VI, 3-pentenoic-γ-anhydride. The important observation is that *no* condensable products appear below about 135°C, *even when the reaction is strongly catalyzed.*

The fact that the Shroud survived the fire of 1532 by 470 years without obvious acceleration of any degradation processes should provide all of the proof necessary that autocatalysis is not a problem. None of the products observed during restoration of the Shroud were truly involved in autocatalysis, and they should cause no fear for the longevity of the cloth.