

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

R. N. Rogers
Fellow (Retired)
University of California, Los Alamos National Laboratory
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Abstract

Based on the facts of chemistry and current storage conditions, the Shroud of Turin is in no danger of catastrophic autocatalytic decomposition. Although it should last for centuries, its life can be extended by keeping it cool; however, it must not be stored too cold.

A "restoration" in June and July 2002 was a precipitate response to the fear that "autocatalytic" processes would lead to imminent, catastrophic degradation of the cloth. It was pursued even though its chief architect and only voice of authority on its chemistry had died. A very large amount of history and chemical information was lost as a result of this operation. It should be a lasting warning to others who leap into irreversible operations they do not understand, but the Shroud has suffered its greatest disaster in at least 470 years.

INTRODUCTION

The Shroud of Turin suffered severe damage during a fire in 1532. It was patched and supported on a backing cloth, and it was preserved in a casket for the next 470 years. As an object of veneration, it was first photographed in 1898, and it has been observed several times since then. It was studied intensively in 1978 by spectroscopy, technical photography, and chemistry. Many reports were written on the observations and condition of the cloth. There was no evidence that the condition of the cloth had changed since the fire of 1532.

I took many photomicrographs of fibers from all parts of the cloth as part of the Shroud of Turin Research Project (STURP), and I made a close study of scorched fibers as part of the development of an hypothesis for image formation. One representative photomicrograph of a scorched fiber is shown in figure 1.



Figure 1: Scorched line n fiber from Shroud sample 1JB.

The figure shows that the surface of the fiber is smooth and transparent. The scorched medulla and deposits of lignin at growth nodes can clearly be seen. The fiber had not been decomposing and it was in no danger of doing so. Many other fibers were investigated with the same conclusion.

Then from a position of complete secrecy, the Shroud was subjected to a vigorous "restoration" in June and July 2002. Those of us who had worked on the scientific aspects of the Shroud for many years were stunned.

Why had this been done? An explanation appears in a book of photographs that were taken after the "restoration" [Ghiberti, G., "Sindone le immagini 2002," Opera Diocesana Preservazione Fede - Buona Stampa, Corso Matteotti, 11 - 10121 Torino]. In section five of the text it explains how Professor Alan Adler had become the most vocal chemist on the Conservation Committee that was responsible for planning for the conservation of the Shroud. It was stated that: "Adler now became the providential link with American researchers and the important results of their investigations." Actually, chemical data were not solicited from American researchers.

The basis for the rush to "restoration" appears in the statement that: "Adler worried about the possibility of the damaging effects of material from the 1532 fire that was trapped under the patches applied by the nuns of Chambéry. When he spoke during the Committee meetings, he did not retreat from the most advanced hypotheses. One of these (certainly not new, as mentioned above, but backed now by the weight of his authority) was to remove the patches and the Holland cloth." Unfortunately, Adler died in June 2000. He had struck fear into the Committee, but he could not be present to control its course.

AUTOCATALYSIS

Autocatalytic chemical reactions are those in which the rate increases as the amounts of reactants decrease, i.e., while the materials are reacting. 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:

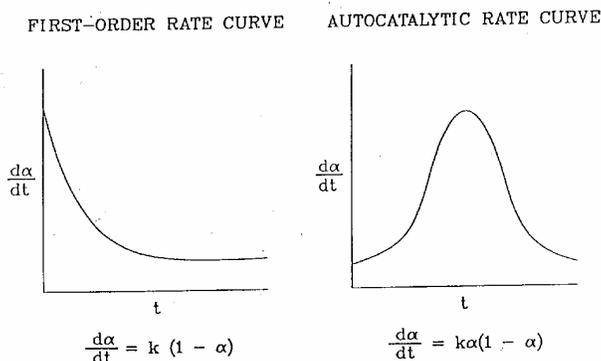
$$\frac{d\alpha}{dt} = k\alpha^p(1-\alpha)^q Ze^{-\frac{E}{RT}}$$

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 ($0K = -273.2^{\circ}C$). 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 2.. 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 chemical decomposition rate of cellulose is essentially zero at room temperature. The decomposition rate of scorched cellulose can not be distinguished from that of pure cellulose, and it is essentially zero at room temperature. Most long-term degradation of cellulose that is observed in archaeological contexts is caused by microbiological attack.



When cellulose is decomposing autocatalytically at high temperature, the rate can be returned to its initial value (essentially zero) by cooling.

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 of the sugar units that

make up the cellulose polymeric chains. 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, and it 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 decompositions predict extremely slow rates, so slow you can call them 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 or microorganisms.

When the crystalline order of cellulose is destroyed by heating, autocatalysis involves a process like "melting with decomposition." The reaction in the cellulose melt is also chemically autocatalytic (see Feigl and Anger below). When the material is cooled below the melting point, autocatalysis stops.

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* 3, 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.

The structure of pure, uncatalyzed, crystalline cellulose 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 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 phase changes, the magnitude of E, and retention of the catalytic product(s).

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 effects of heating cellulose 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*.

If catalytic products are gases, they can escape from the reacting zone after cooling. Superheated steam does not exist at normal temperatures, and the only important autocatalytic process in cellulose stops until another heating episode. There is no "memory effect." The Shroud should be as stable at room temperature as any other sample of linen.

Although the primary decomposition process of all carbohydrates, including cellulose (linen), is dehydration, 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 difficult to determine the difference between adsorbed water and water of reaction. It may require measurements involving kinetic isotope effects with deuterium.

More detailed studies have shown that the major secondary products of the thermal decomposition of cellulose are formaldehyde, 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. Indeed, formaldehyde, furfural, and hydroxymethylfurfural are reducing agents, antioxidants. Furfural inhibits the growth of molds and yeasts. Scorched areas are less likely to show microbiological attack.

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 study was the rapid, *catalyzed* decomposition of pure levulose. The sugar units

in linen are glucose, a similar hexose. 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 important observation was that *no* condensable products appeared below about 135°C, *even when the reaction was strongly catalyzed*. This kind of catalyzed reaction is similar to that responsible for the destruction of books that are made with cheap, acid paper. Claiming analogy between such books and the Shroud is mischievous.

Adler and Schwalbe made the following comment: "Previous chemical reactions on the cloth, e.g., the retting process in manufacture of the linen, the known historic fire and its extinguishment, and previous display and storage procedures, have left a variety of chemical structures on the surface that can act as oxidants and also as catalysts. For example, the acidic structures produced by previous oxidative activity can strongly promote various types of autocatalysis" [A. D. Adler and L. A. Schwalbe, "Conservation of the Shroud of Turin," Shroud Spectrum International, No. 42, December 1993, Indiana Center for Shroud Studies]. Evidence does not support that claim.

I have not been able to observe any chemical autocatalysis in cellulose or previously scorched cellulose at normal temperatures. Observations and descriptions of the Shroud through the 470 years since the fire of 1532 do not support fear of catastrophic decomposition of the cloth: They give direct evidence for the stability of the Shroud. However, if Shroud deterioration is still a worry, one practical way to slow the rate is to keep it cold. That also has the advantage of reducing microbiological attack, but too low 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. Severe freezing could damage the cloth and image.

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°C 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. Chemical considerations predict a very long lifetime for the Shroud at room temperature, barring too many "restorations."

Linen heating experiments:

It is extremely unfortunate that the "restoration" was pursued without any effective communication with experts on the chemical properties of the materials. Much information has been available since early 1977, and much more has been available since the Shroud of Turin Research Project (STURP) scientific observations of 1978.

In preparation for the meeting at which STURP was organized, I studied all available photographs of the Shroud for chemical information, and I made a presentation on the chemical information that could be gained from the effects of the fire of 1532 [Rogers, R. N., "Chemical Considerations Concerning the Shroud of Turin," pp. 131-135, in Kenneth

Stevenson (Ed.), *1977 United States Conference of Research on The Shroud of Turin*, 23-24 March 1977, Albuquerque, NM, USA, Holy Shroud Guild, 294 East 150 St., Bronx, N. Y. 10451]. I had noticed that the fire of 1532 caused scorches to intersect areas of pure image, pure blood, and blood on image. In addition, water had been used to put out the fire, and water had migrated through some zones of scorching at intersections. A mass of chemical information could be obtained by observing such zones.

I did a number of scorching experiments on linen to observe the effects of heating/charring on pigments and expected media. One example can be seen at <http://www.shroud.com/pdfs/rogers2.pdf> in both visible and ultraviolet light.

All paints were changed by heat and/or the chemically reducing and reactive pyrolysis products (formaldehyde, furfural, organic acids, CO, etc.). Some Medieval painting materials become water soluble and they would have moved with the water that diffused through parts of the cloth at the time of the fire. Observations on the Shroud in 1978 showed that nothing in the image moved with the water. Unfortunately, there was insufficient time and equipment for an exhaustive observation of scorch intersections in 1978. There seemed to be no reason to worry: Future observations could answer all of our questions. The restoration has now destroyed all of the important areas. What might approach 2000 years of chemical history has been lost forever.

Summary:

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 significant problem. There is no legitimate fear for the longevity of the cloth.