

Glycobiology Conference 2017: Effect of temperature on photochemical and thermal changes in calf skin collagen solutions at physiological pH - Julian Menter - Morehouse School of Medicine

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Mammalian dermal collagen is in close contact with extracellular matrix (ECM) molecules, most prominently hyaluronan (HA) and associated proteoglycan (PG) molecules. The HA – PG system forms a complicated network that provides support for resting tissues and can facilitate wound healing and act as signaling molecules. We have previously used fluorescence of type I collagen tyrosine residues to study the ground- and excited state chemistry that results in structural and molecular alterations that could have significant (deleterious) effects. We are now turning our attention to the effect of surrounding ECM on collagen. Our strategy is to build up the ECM system starting with the core HA molecule, first adding glycosaminoglycans, (GAGs) then PG model compounds in solution. In this communication, we present the results of the effect of hyaluronan on collagen photo stability as evidenced by the rate of di-tyrosine formation as measured by di-tyrosine fluorescence ($\lambda_{ex} = 325 \text{ nm}$, $\lambda_{em} = 400 \text{ nm}$). The experiments reported here consisted of model solutions of type I calfskin collagen (1 mg/ml) + hyaluronan (2 mg/ml) in 0.1 M phosphate buffer, pH 7.4 solutions were irradiated in a thermostatted quartz cuvette with a 4 W low pressure Hg lamp (main emission wavelength 254 nm superimposed on a low continuum). Photochemistry is that the branch of chemistry concerned with the chemical effects of sunshine. Generally, this term is employed to explain a reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), light (400–750 nm) or infrared (750–2500 nm). In nature, photochemistry is of immense importance because it is that the basis of photosynthesis,

and therefore the formation of vitamin D with sunlight. Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high energy intermediates that can't be generated thermally, thereby overcoming large activation barriers during a short period of your time, and allowing reactions otherwise inaccessible by thermal processes. Photochemistry is additionally destructive, as illustrated by the photodegradation of plastics. Photoexcitation is that the initiative during a photochemical process where the reactant is elevated to a state of upper energy, an excited state. The primary law of photochemistry, referred to as the Grothuss–Draper law (for chemists Theodor Grothuss and John W. Draper), states that light must be absorbed by a chemical substance so as for a chemical reaction to require place. consistent with the second law of photochemistry, referred to as the Stark-Einstein law (for physicists Johannes Stark and Albert Einstein), for every photon of sunshine absorbed by a chemical system, no quite one molecule is activated for a chemical reaction, as defined by the quantum yield. Photochemical reactions require a light-weight source that emits wavelengths like an electronic transition within the reactant. Within the early experiments (and in everyday life), sunlight was the sunshine source, although it's polychromatic. Mercury-vapor lamps are more common within the laboratory. Low mercury vapor lamps mainly emit at 254 nm. For polychromatic sources, wavelength ranges are often selected using filters. Alternatively, laser beams are usually monochromatic (although two or more wavelengths are often obtained using nonlinear

optics) and LEDs have a comparatively narrowband which will be efficiently used, also as Rayonet lamps, to urge approximately monochromatic beams. Schlenk tube containing slurry of orange crystals of Fe²⁺ (CO)₉ in ethanoic acid after its photochemical synthesis from Fe(CO)₅. The mercury lamp (connected to white power cords) are often seen on the left, set inside a water-jacketed quartz tube. The emitted light must in fact reach the targeted functional group without being blocked by the reactor, medium, or other functional groups present. For several applications, quartz is employed for the reactors also on contain the lamp. Pyrex absorbs at wavelengths shorter than 275 nm. The solvent is a crucial experimental parameter. Solvents are potential reactants and for this reason, chlorinated solvents are avoided because the C-Cl bond can cause chlorination of the substrate. Strongly absorbing solvents prevent photons from reaching the substrate. Hydrocarbon solvents absorb only at short wavelengths and are thus preferred for photochemical experiments requiring high energy photons. Solvents containing unsaturation absorb at longer wavelengths and may usefully filter short wavelengths. For instance, cyclohexane and acetone "cut off" (absorb strongly) at wavelengths shorter than 215 and 330 nm, respectively. Within the case of photochemical reactions, light provides the energy of activation. If laser light is used, it's possible to selectively excite a molecule so on produce a desired electronic and vibrational state. The absorption of a photon of sunshine by a reactant molecule can also permit a reaction to occur not just by bringing the molecule to the required energy of activation, but also by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction path, as described by the Woodward–Hoffmann selection rules. Some photochemical reactions are several orders of magnitude faster than thermal reactions; reactions as fast as 10–9 seconds and associated processes as fast as 10–15 seconds are often observed. The photon are often absorbed directly by the reactant or by a

photosensitizer, which absorbs the photon and transfers the energy to the reactant. The other process is named quenching when a photoexcited state is deactivated by a chemical reagent. Most photochemical transformations occur through a series of straightforward steps referred to as primary photochemical processes. One common example of those processes is that the excited state proton transfer. Temperature was varied from 8–62 °C. The rates of dityrosine formation were monitored by the rise in 325/400 nm fluorescence with time. The effect of HA was determined by comparing the rates of fluorescence increase companion solutions of collagen + HA, expressed as the rate of R = collagen/collagen + HA as functions of temperature. Below the melting temperature T_m, R > unity and at 35°C and > 50°C, R < 1.0. Above 50°C, there is a rapid increase in di-tyrosine formation, and R ~ unity. Our interpretation is that at lower temperatures, where the helical form exists, collagen is stabilized by HA; above the melting temperature, collagen is destabilized. At T > ~ 50°C, collagen exists as a denatured coil facilitation, with an activation energy that suggests hydrogen bond breakage.

Biography

Julian M Menter has received his PhD degree in Chemistry from the George Washington University in 1969. He has completed a Postdoctoral Fellowship with Prof. Dr. Theodor Foerster at the Institut fuer physikalische Chemie der Universtiaet Stuttgart, Germany. Subsequently, he was at the University of Alabama, Birmingham, and the VA Medical Center (Atlanta). He currently serves as Research Professor of Biochemistry at Morehouse School of Medicine. He is recognized internationally for his work in areas of collagen photochemistry and melanin photobiology as pertaining to redox reactivity.

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