The Photochemistry of Sunscreens

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There is a new public awareness of the damaging effects of overexposure to the sun. Many of us take advantage of the effects of chemical sunscreens to lengthen the time we can safely spend outdoors without risking short-term skin damage in the form of sunburn or long-term damage in the form of skin cancer. The action of sunscreens to prevent the harm that can be caused by excess exposure to ultraviolet radiation offers an interesting application of molecular excited states and photochemistry.

The harmful effects of solar radiation are caused predominantly by the ultraviolet region of the electromagnetic spectrum, which can be divided into three regions. UV-A is the least biologically harmful type of ultraviolet light, as it corresponds to the low-energy region of the UV, between 320 and 400 nm. Most of the UV-A in sunlight reaches the earth's surface (1). Much of the higher-energy UV-B (280–320 nm) and all of the highest-energy UV-C (200–280 nm) is filtered out by the earth's atmosphere, although continued deterioration of the ozone layer could change that (1). Overexposure to UV-B causes most skin cancer and has also been linked to a suppression of the human immune system, although recent research has shown that sunscreens that block only UV-B (and not UV-A) do not adequately protect us from the risk of skin cancer (1–3).

To understand how sunscreens work, one must understand how molecules interact with light energy. Absorption of light by a molecule is associated with the part of its structure called a chromophore, which may or may not encompass the whole molecule (4). For organic molecules the chromophores that are responsible for absorption of ultraviolet light are generally associated with delocalized $\pi$-electrons in conjugated systems. In general, when a molecule absorbs a photon whose energy is high enough, an electron is promoted from a lower energy level to a higher energy level. The molecule is said to go from its ground state to an excited state (see Fig. 1). The most common excited state for organic molecules is the first singlet excited state, in which the promoted electron is still spin-paired with the one left in the lower energy level.

Once in the excited state, the molecule has several available pathways, which are outlined in Figure 1.

1. The molecule can emit a photon and return to the ground state; this process is called fluorescence.
2. The molecule can return to the ground state by emitting the energy thermally through a series of vibrational transitions; this is called nonradiative decay or vibrational relaxation (4, 5).
3. The molecule can undergo some type of reaction from the excited state, which is generally termed photochemistry.
4. Finally, the molecule can convert to a lower energy excited state—typically the triplet state, in which the electrons cease to be spin paired. The lower energy excited state can in turn revert to ground state in either a radiative (phosphorescence) or nonradiative (vibrational) decay, or it can also undergo photochemistry.

Which of the many pathways described above predominates depends on the relative rates of each process, the favored path being the one with the most rapid rate. The relative rates depend on the nature of the chromophore and the particular structure of the molecule in question.

The photochemistry and photoproducts of DNA, as well as their resulting mutagenic potential, have been discussed in great detail by Taylor (3). The majority of products result from a photochemical reaction of the lower-energy excited state described above. Humans' natural protection mechanism against the effects of exposure to UV light involves specialized skin cells called melanocytes (6, 7). When skin is irritated by exposure to UV light, melanocytes produce a black pigment called melanin and distribute it through the skin. The presence of melanin results in a tanned appearance and protects the skin by absorbing ultraviolet radiation, thus preventing the type of photochemical reactions that produce skin damage.

Protection against UV light can also be accomplished through the use of topically applied chemical sunscreens. The sunscreens that are commercially available function in one of two ways. Substances such as zinc oxide and titanium dioxide offer physical protection in that they are opaque enough to reflect and scatter the incident radiation. Photon-absorbing agents function by absorbing radiation in the ultraviolet region and then undergoing very rapid vibra-
tional relaxation back to the ground state (8–11). Once in the ground state, these molecules can absorb another photon to repeat the process, thereby effectively shielding the skin from damage by UV radiation. Any molecule for which vibrational relaxation to the ground state is the fastest pathway can act as a sunscreen. However, only 14 different substances are commonly used in sunscreen preparations in the United States. Structures for the most common ones can be found in Table 1 (8–10).

The structural similarities of these compounds are evident. All are substituted aromatic compounds with a high degree of conjugation, which allows them to absorb in the appropriate region for protection against ultraviolet radiation (4, 5, 8). Historically the first commercially available photon absorbing chemical sunscreen was para-aminobenzoic acid (PABA), which absorbs strongly in the UV-B region of the spectrum (11). PABA itself is not especially oil soluble, thus making it unappealing for the formulations normally associated with skin lotions. Therefore various PABA esters (which are more oil soluble) are used. Both PABA and PABA esters cause a photoallergic response in 1–2% of the population (10), so PABA-free sunscreen preparations typically have one or more of the other substances found in Table 1 as their active ingredient. The cinnamate esters, oxybenzone, and avobenzone are also highly oil soluble and have the additional protective advantage that they also absorb strongly in the UV-A range, offering better overall protection (8, 11). The salicylates tend to have a low molecular absorptivity coefficient, meaning that a higher concentration is needed in order to obtain the same protection afforded by a lower concentration of a different substance (9).

The efficacy of a sunscreen is described on the label by the “sun protection factor” or SPF, which is defined as the UV energy required to produce a minimal erythema (sunburn) dose (MED) on protected skin divided by the UV energy required to produce an MED on unprotected skin (9, 10):

$$\text{SPF} = \frac{\text{MED protected}}{\text{MED unprotected}}$$

The “dose” can be measured in intensity of light or in length of exposure. The latter is the more common method of SPF determination (9, 12). In this manner,
each individual’s particular sensitivity to ultraviolet radiation is taken into account in the generalized SPF number. There are two ways in which to increase the SPF of a particular sunscreen preparation. One can increase the concentration of the active photon-absorbing ingredient. As is evident from Beer’s law, the higher the concentration, the greater the number of photons absorbed. One can only take this so far, however, before the concentration becomes high enough to be irritating to the skin. Combining two or more of the substances in Table 1 in the formulation is a common way to increase the SPF value of a sunscreen preparation because the effective photon absorption is roughly additive.

Most of us have experienced a sunburn, and most of us have relied upon sunscreens to prevent it. The chemistry involved in the action of sunscreens, particularly when coupled to the photochemistry of DNA (3), is a relevant introduction to the interaction of light energy with molecules, the behavior of molecular excited states, and the effects of concentration and absorption.

Literature Cited