Photosensitized *cis-trans* Isomerization of Jojoba Wax

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ABSTRACT

Jojoba wax solutions were irradiated at wavelengths longer than 366 nm, in the presence of sensitizers, at room temperature. *Cis-trans* isomerization took place only with sensitizers with triplet energy greater than 68 kcal/mol. Quantum yields were low and a conversion of up to 25% of the *trans* isomer was achieved at the photostationary state.

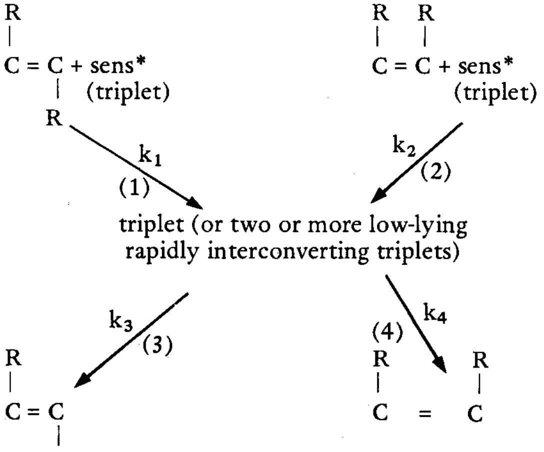
INTRODUCTION

The potential uses of jojoba wax and its present application as a component in cosmetic formulations prompted us to investigate its behavior with respect to *cis-trans* isomerization, both thermally and photochemically. Relatively high temperatures are required to attain an effective thermal conversion to *trans* isomers (1). Photoisomerization of the two *cis* isolated double bonds present in the wax molecules, on the other hand, may take place at low temperatures and therefore affect the properties of products containing jojoba wax, both on the shelf and during application.

The direct photoisomerization of isolated carbon-carbon double bonds is unimportant in the context referred to above, as it requires short wavelength ultraviolet (UV) irradiation (under 200 nm). Photosensitized reactions may be important because sensitizing substances may be part of formulations for the skin.

RESULTS AND DISCUSSION

Seheme 1, originally suggested by Hammond and coworkers (2) as the general mechanism for the photosensitized process, has found wide application (3).



SCHEME 1

Reaction 1, although nonexistent at the inception of the photoisomerization of jojoba wax, becomes important as the concentration of *trans* isomers increases until the photostationary state is reached. For high triplet energy sensitizers, which we found to be the only effective ones with jojoba wax, triplet energy transfer takes place at diffusion-controlled rates, thus the k_1 to k_2 ratio is nearly 1. The composition of the photostationaty state, therefore, essentially depends on the relative rates of decay of the intermediate triplet (or triplets) according to path 3 or 4:

$$K_{stat} = \left(\frac{trans}{cis}\right)_{stat} = \frac{k_3}{k_4}$$

Table I summarizes the result found for sensitizers covering a wide range of triplet energy values (E_t). Photosensitizers with E_t lower than 68 kcal/mol (285 kJ/mol) were ineffective as isomerization promoters. This threshold E_t value seems to be only a necessary condition, as acrolein and diphenylamine, both with higher E_t, did not cause isomerization.

Testa found in a similar study (4) that methyl oleate isomerizes to a photostationary state containing 23% of *trans* isomer in benzene solution in the presence of benzophenone as sensitizer. The quantum yield was $\phi = 0.34$. The conversion we found was similar, but the quantum yield was much lower with jojoba wax in petroleum ether solutions. It is reasonable to discard the participation of benzene as sensitizer, as much shorter wavelengths would be needed for benzene excitation. The reduced quantum yields obtained with jojoba wax are possibly due to molecules being larger and more rigid than methyl oleate.

The triplet energy of jojoba wax (69 kcal/mol) as obtained by extension of Hammond's method (5) is less than those of simple olefins (82 kcal/mol for 2-butene), but, of course, higher than those of conjugated olefins (59 kcal/mol for 1,3-pentadiene).

TABLE I

Equilibrium Constants (K) and Quantum Yield (ϕ) for the Photosensitized *cis-trans* Isomerization of Jojoba Wax[a]

Sensitizer[b]	E_t (kcal/mol)	K	ϕ
Benzophenone	68.5	0.32	0.014
2-Chlorobenzaldehyde	69.6	0.30	0.054
Benzaldehyde	71.3	0.24	0.044
Acetophenone	73.6	0.17	0.011

[a] Triplet energies E_t were taken from reference 6.

[b] The following photosensitizer (E_t) were also tried, but no *cis-trans* isomerization took place: benzil (53.7), α-acetonaphthone (56.4), quinoline (62.0), anthraquinone (62.4), ethyl acetoacetate (66.0), acrolein (ca. 69), and diphenylamine (72).

EXPERIMENTAL

Jojoba wax (Apache Reserve) was purified as described elsewhere (1). Photosensitizers were commercially available organic laboratory reagents. Olefin-free petroleum ether (bp 60-80 C) was prepared by treating the solvent with concentrated sulfuric acid, washing with water and drying over anhydrous magnesium sulfate. Calibration of the infrared (IR) analytical method of determination of *trans* double bond content was described elsewhere (1).

Photoisomerization runs were made as follows: a solution of jojoba wax in petroleum ether (5-10% w/v), containing ca. 0.02 mol/L of sensitizer, was degassed with argon and placed in a set of well-covered, 1-cm path, fused Pyrex cells, under argon blanketing. The cells were placed in a bath at 18 C and were rotated around the UV source to ensure uniform irradiation. The source was a Hanau Heraeus TQ-150-Z3 lamp with a filter cutting out wavelengths under 366 nm. After a certain irradiation time, one

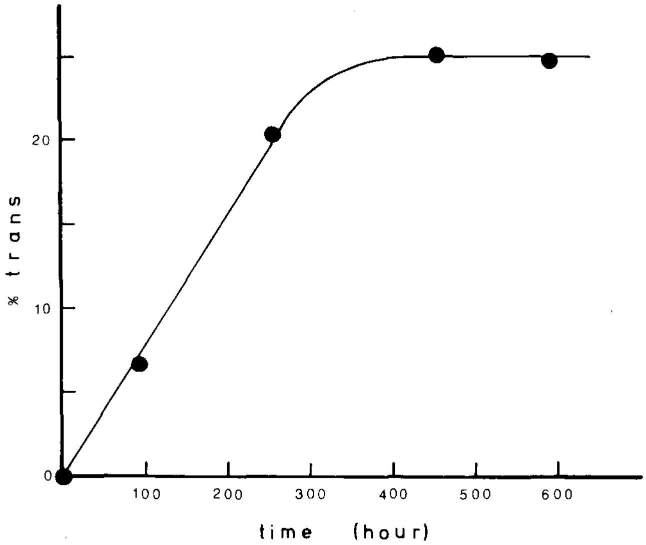


FIG. 1. Photoisomerization of jojoba wax in the presence of benzophenone.

of the cells was opened and the intensity of the IR peak at 970 cm^{-1}, typical of the *trans* isomer (7), was measured in a 0.2-mm path KBr cell, in a 357 Perkin-Elmer IR spectrophotometer. Quantum yields were referred to a potassium ferrioxalate actinometer (8). A typical run appears in Figure 1.

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