Kinetics of Pheophytin-A Photodecomposition in Extra Virgin Olive Oil

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The amount of pheophytin-A in extra virgin olive oil was determined by reverse-phase high-performance liquid chromatography (HPLC) with chlorophyll-A as an internal standard. The kinetics of pheophytin-A photodecomposition at 15, 40 and 50°C at three different luminous energies were studied. The pheophytin-A photodecomposition process develops according to a first-order reaction. From the Arrhenius' straight lines, it appears that the incident luminous energy does not change the activation energy but increases the reaction frequency factor.

KEY WORDS: Activation energy, chlorophyllian pigments, extra virgin olive oil, first-order reaction, frequency factor, HPLC analyses, kinetic constant, luminous energy, pheophytin-A, photodecomposition.

The color of virgin olive oil is mainly due to carotenoid and chlorophyllian pigments, whose content depend upon many factors including plant variety, soil and climatic conditions, fruit ripeness and oil extraction method (1).

This paper reports a study on the pheophytin-A photodecomposition in extra virgin olive oil, keeping into account the influence of temperature and light intensity on the kinetic constant of this reaction.

Preliminary HPLC analyses, made on extra virgin olive oils from the 1989–90 production year, showed that the prevailing chlorophyllian pigment is pheophytin-A in the 3 to 12 ppm range. On a preliminary basis, it was also found that chlorophyll photodecomposition occurs quickly; in fact, a 6 ppm chlorophyll-A content is fully degraded in less than 1 h if the oil is exposed to radiation from a 40-W tungsten source at 15°C (A. Serani and D. Piacenti, unpublished data). The role of oxygen in pheophytin-A photodecomposition could be excluded because the reaction kinetics did not change appreciably when a fully degassed oil sample was submitted to the same test conditions.

MATERIALS AND METHODS

Sampling. Commercial extra virgin olive oil with a 7.1 ± 0.2 ppm pheophytin-A content was used as a sample.

Photodecomposition reaction. Vials (10-mL), each filled with 7 g of oil, were arranged inside a forced-ventilation, thermostatically controlled room and submitted to different light radiations (40, 60 and 100 W, tungsten sources) and temperatures (15, 40 and 50°C).

HPLC analyses. A Perkin-Elmer series 400 chromatograph, equipped with an LC-95 UV/VIS detector and two series-mounted Supelco columns (Bellefonte, PA) (25 cm 5/LC-18 and 16 cm 3/LC-18), was used for chromatography. The gradient was acetone:water (75:25) to acetone in 30 min at a flow rate of 1.6 mL/min. The oil was diluted with 50% acetone, 0.01 mg of Chlorophyll-A (internal standard) was added, and the solution was injected with a 10-μL loop.

Signals were detected at 670 nm and were assigned by comparison with reference standards [chlorophyll-A and chlorophyll-B, Aldrich Chemical Company (Milwaukee, WI); pheophytins were prepared from chlorophylls by reaction with HCl (2)] and literature data (3,4).

RESULTS AND DISCUSSION

Figure 1 shows the decline of the pheophytin-A content in the oil as a function of temperature and light conditions. The degradation of pheophytin-A has zero asymptotic exponential development, typical of unbalanced reactions. The semi-logarithmic plot (Fig. 1) gives good linearization of the experimental points. Such linearization allows the calculation of the kinetic constant (k) of pheophytin-A photodecomposition under the temperature and light conditions adopted, thus showing that the reaction occurs according to first-order kinetics:

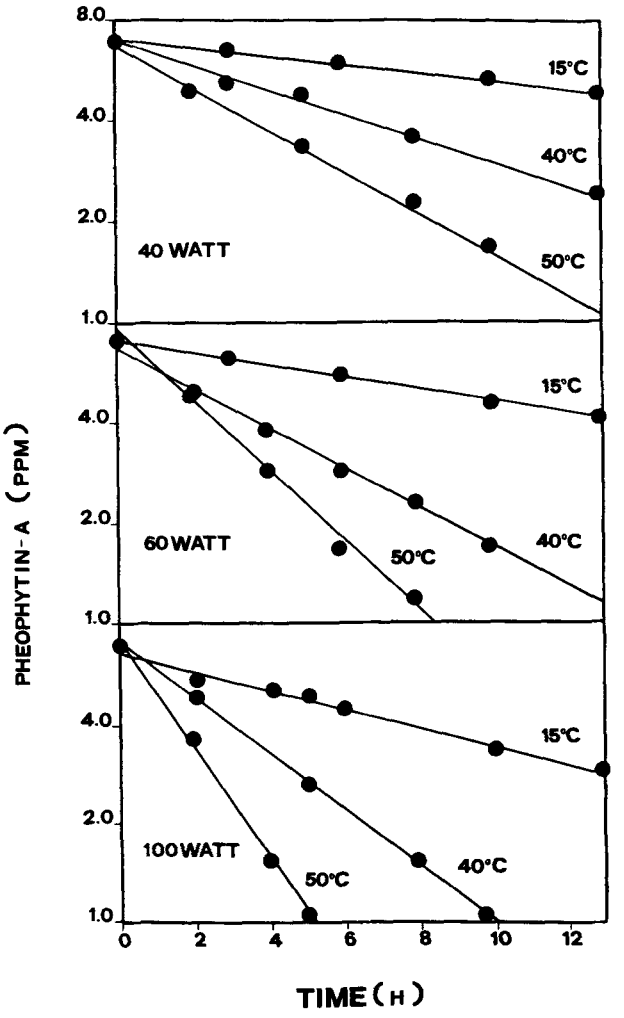

FIG. 1. Pheophytin-A concentration during photodecomposition time under 40, 60 and 100 W radiation.

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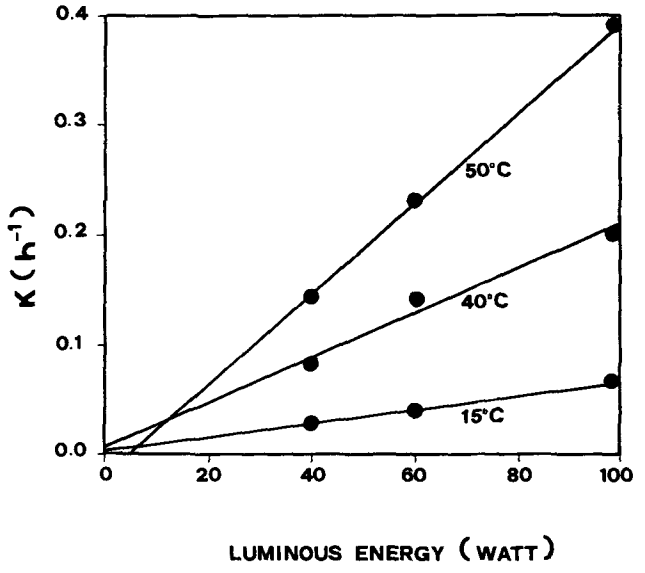

FIG. 2. Values of the kinetic constant *versus* luminous energy at different temperatures.

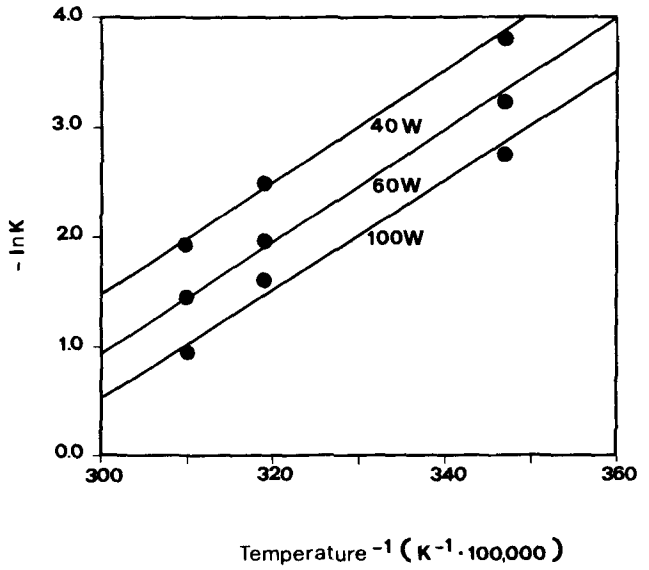

FIG. 3. Arrhenius' straight lines for the pheophytin-A photodecomposition.

Pheophytin-A → decomposed pheophytin-A

$$d[F]/dt = -k[F] \quad [1]$$

$$[F] = [F]_0 \, e^{-Kt} \quad [2]$$

where: [F] = pheophytin-A conc. at time t; $[F]_0$ = pheophytin-A conc. at time t = 0. The above equations show that for constant incidental light energy, pheophytin-A photodecomposition depends upon the initial pheophytin-A concentration.

Figure 2 shows that the kinetic constants, calculated from the linearized equations, are directly proportional to the luminous energy and that the intercept of the straight lines is near the origin. These experiments show that pheophytin-A photodecomposition gives products that do not affect the reaction order and that temperature is not an important factor in decomposition when there is no light.

By plotting the logarithm of the kinetic constant against the inverse of the temperature, the frequency factors and the activation energy for the pheophytin-A decomposition can be calculated (Fig. 3). This plot clearly shows that the three straight lines are parallel and that the incident luminous energy affects the frequency factor, thus increasing the number of pheophytin-A molecules available for photodecomposition, but leaving the activation energy unchanged. We can, therefore, state that under the conditions adopted, light energy does not act as a catalyst but as an element sharing in the decomposition reaction.

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