# Kinetic Studies on the Thermal $Z/E$-Isomerization of $C_{40}$-Carotenoids

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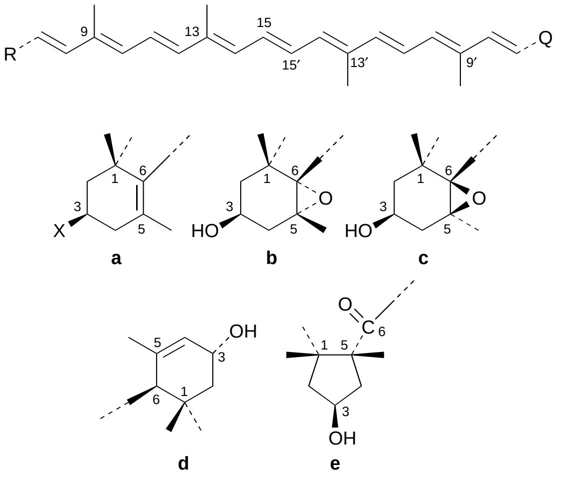
The kinetics of thermal $Z/E$-isomerization among all-$E$-, 9(9′)$Z$-, 13(13′)$Z$- and 15$Z$-isomers of zeaxanthin **1**, violaxanthin **2**, capsorubin **3**, capsanthin **4** and lutein epoxide **5** are studied at 333.4–368.4 K.

The thermal isomerization of **1–5** in pyridine or benzene over the temperature range 333–368 K yielded complex equilibria[25–26] governed by first-order forward and reverse elementary steps.[28–29] In compliance with the analytical approach, four models (I–IV) were used to describe the mechanisms by which the $Z$- and all-$E$-isomers were interconverted.

Model I was used to describe the thermal $Z/E$-isomerization when the formation or the consumption of the $Z$-isomers with high *cis*-peaks (13$Z$, 13′$Z$ and 15$Z$) was monitored by UV–VIS-spectrophotometry:[1,22,25–26,28–30]



**a** **b** **c** **d** **e**

**1** Zeaxanthin (R = Q = **a**, X = OH) **2** Violaxanthin (R = Q = **b**)
**3** Capsorubin (R = Q = **e**) **4** Capsanthin (R = **a**, X = OH, Q = **e**)
**5** Lutein epoxide (R = **b**, Q = **d**)

$$\text{All-}E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 13[13'(15)]Z$$

Model II consists of two reversible concurrent reactions[11,23,25,32] and is represented by the following systems, typical of a symmetrical carotenoid:

$$13Z \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{All-}E \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 15Z$$

and an unsymmetrical carotenoid.

$$13Z \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{All-}E \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 13'Z$$

The reactions leading to equilibria were followed by HPLC.

Model III was used for more complex systems containing All-$E$-, 13$Z$-, 15$Z$-, 9$Z$- and di-$Z$-isomers:[22]

$$\begin{tikzcd} 13Z \arrow[r, shift left, "k_{-1}"] & \text{All-}E \arrow[l, shift left, "k_1"] \arrow[r, shift left, "k_2"] \arrow[d, shift left, "k_3"] & 15Z \arrow[l, shift left, "k_{-2}"] \\ & 9Z+\text{di-}Z \arrow[u, shift left, "k_{-3}"] & \end{tikzcd}$$

(mixed peak)

For the evaluation of the rate constants the respective formation and consumption of the 9$Z$-and di-$Z$- isomers were considered together.

Model IV was based on the most detailed analysis of the thermal isomerization mixtures.

**Table 7** Arrhenius and activation parameters of the reversible isomerization of the (all-$E$)-**1** to (13$Z$)-**1** and (15$Z$)-**1** using the rate constants obtained in the simulation of the reaction mechanism defined by models II and III; $T_{\text{av.}}$ = 357.4 K[a]

| Rate constant | log ($A$/s$^{-1}$) | $E_A$/kJ mol$^{-1}$ | $\Delta H^\ddagger$/kJ mol$^{-1}$ | $\Delta S^\ddagger$/J mol$^{-1}$ K$^{-1}$ | $\Delta G^\ddagger$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| *Model II* | | | | | |
| $k_1$ | 11.53 (0.31) | 104.6 (3.1) | 101.6 (3.1) | −34.1 | 113.8 |
| $k_{-1}$ | 10.68 (0.16) | 97.0 (1.3) | 94.0 (1.4) | −50.6 | 112.1 |
| $k_2$ | 12.85 (0.41) | 118.6 (4.6) | 116.9 (5.1) | −5.1 | 118.7 |
| $k_{-2}$ | 13.39 (0.61) | 115.6 (11.1) | 112.6 (11.2) | −1.6 | 112.0 |
| *Model III* | | | | | |
| $k_1$ | 11.55 (0.48) | 104.9 (6.0) | 102.0 (6.0) | −33.6 | 114.0 |
| $k_{-1}$ | 10.60 (0.26) | 96.6 (2.4) | 93.6 (2.4) | −51.8 | 112.1 |
| $k_2$ | 12.77 (0.42) | 118.0 (4.8) | 115.1 (4.8) | −10.3 | 118.8 |
| $k_{-2}$ | 13.22 (0.67) | 114.5 (10.8) | 111.6 (10.8) | −1.8 | 118.2 |
| $k_3$ | — | — | — | — | — |
| $k_{-3}$ | — | — | — | — | — |

[a]Data in parentheses are the standard deviations. Arrhenius and activation parameters of reactions (3), (−3) and (4), (−4) are not given because of significant error. Model IV was used, with relatively high deviation, to calculate $k_3$, $k_{-3}$ and $K_4$

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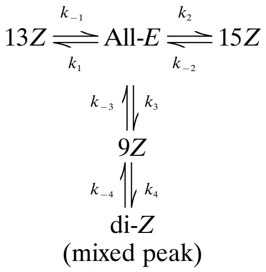

Rate constants were calculated using the program package ZITA for advanced kinetic simulations;[24] that is, the ordinary differential equations (ODE) of the kinetic models were solved by the GEAR method.[33] Curve fitting was carried out applying the Marquard–Levenberg method.[34]

The Arrhenius parameters were calculated by non-linear parameter estimation with statistical weights $w_i = 1/k_i^2$. Values of $E_A$, $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta G^\ddagger$ and $A$ were obtained from the rate constants determined on the basis of Models I–IV.

The Arrhenius and activation parameters for thermal interconversions among (all-*E*)-**1**, (13*Z*)-**1** and (15*Z*)-**1**, calculated from the rate constants obtained in simulation of the different models (II–IV), are listed in Table 7.

Techniques used: UV–VIS spectroscopy, HPLC, column chromatography

References: 48

Tables: 12

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