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Biophysical Chemistry 83 (1999) 179–184

Biophysical Chemistry

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Why is the human visual system sensitive only to light of wavelengths from approximately 760 to 380 nm? An answer from thermochemistry and chemical kinetics

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Received 13 September 1999; received in revised form 1 November 1999; accepted 1 November 1999

Abstract

The range of visible light has been explained by the knowledge available of gas-phase thermochemistry and chemical kinetics. The C, C–π bond dissociation energy at the 11 and 12 positions of the rhodopsin complex is estimated to be approximately 37.4 ± 1.5 kcal/mol. This energy is just equivalent to wavelength of the red limit of the visible light. The photons of the violet limit (approx. 75.2 kcal/mol) can break the weakest C–C and H–C bonds in important species involved in the photo-induced *cis–trans* isomerization cycle and can stop the visual cycle. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Bond dissociation energy; C, C–π bond; Vitamin A; Retina; Rhodopsin; *cis–trans* isomerization; Visual cycle

1. Introduction

The human visual system is sensitive only to a very small portion of the electromagnetic spectrum, i.e. the wavelengths of visible light are only from approximately 760 (the red limit) to 380 (the violet limit) nm [1–5]. Why is this? This work will give an answer based on the information of bond dissociation energies (BDEs).

The five chemical steps involved in photoreception are described as Fig. 1 [6–11]. The first step is to form a complex, rhodopsin. A photon is absorbed by the complex, and the resulting excited species is then isomerized to an all-*trans* bathorhodopsin complex (step 2). The all-*trans* form is not stable, which results in the release of a proton (step 3) giving metarhodopsin II. After approximately 1 s, the later complex dissociates into an all-*trans*-retinal molecule plus opsin (step 4). The all-*trans* isomer cannot fit into the protein opsin due to its molecular shape, but the all-*trans*-retinal can be isomerized back to the 11-

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PII: S0301-4622(99)00137-4

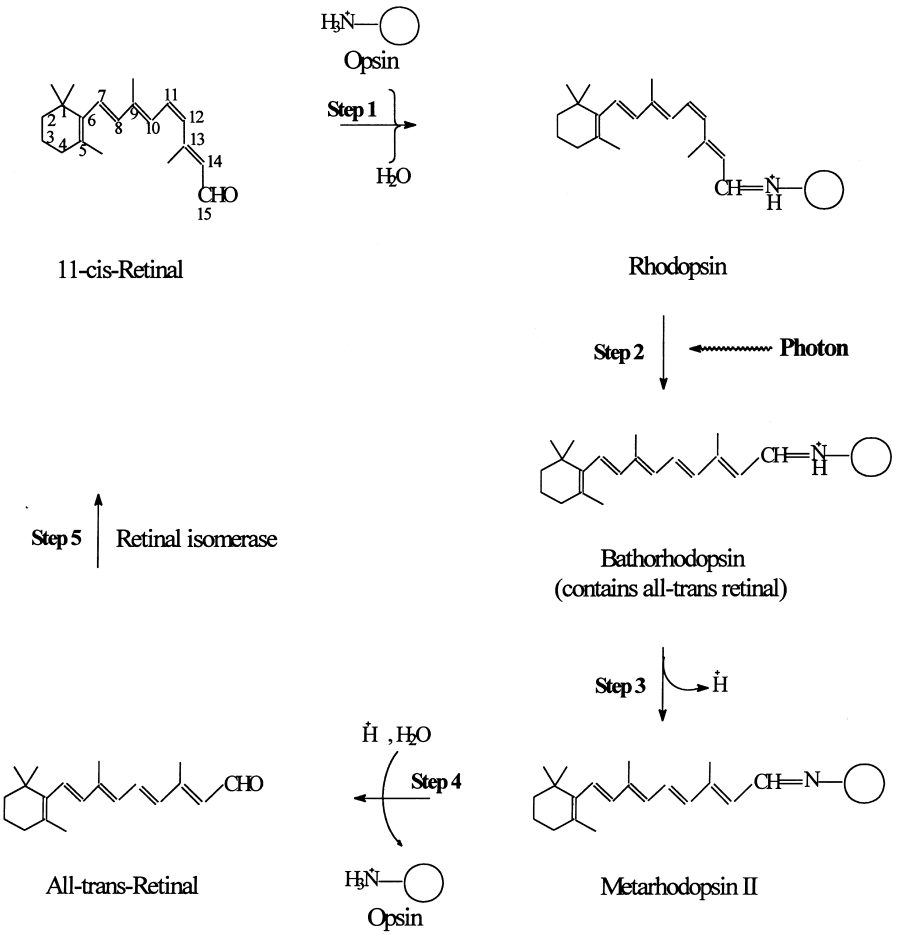

Fig. 1. Chemical cycle of human vision.

cis-retinal in the dark by the enzyme retinal isomerase (step 5). The resulting 11-*cis*-retinal can be used to resynthesise the visual pigments (rhodopsin) and to go to the next *cis–trans* isomerization cycle so that vision continues.

The primary step in the vision cycle is photon absorption followed by excitation and *cis–trans* isomerization of rhodopsin. In essence, a photon has been converted into atomic motion (conformational changes) in the vision cycle. The uncoiling of the molecule triggers a nerve impulse to the brain, which occurs in approximately 1 ms.

Note that there is a C, C–π bond at the 11 and 12 positions of rhodopsin. Which wavelength can excite this π bond? Clearly, the photon energy must be greater than or equal to the C, C–π BDE at the least. The red limit observed by the naked eye is strongly dependent on the C, C–π BDE, DH°(C, C–π at 11–12). In order to have a better understanding of the chemistry of vision, we must estimate this π BDE.

2. The C, C–π BDE and the red limit

The π BDE can be simply predicted [12–14]. Design a thermochemical cycle that consists of three steps, as presented in Fig. 2. Supply an energy, *DH°* (C, C–π, at 11–12), and break the π bond in the rhodopsin, which gives a bi-radical at the 11 and 12 positions (Fig. 2, step 1). The bi-radical takes two hydrogen atoms from a hy-

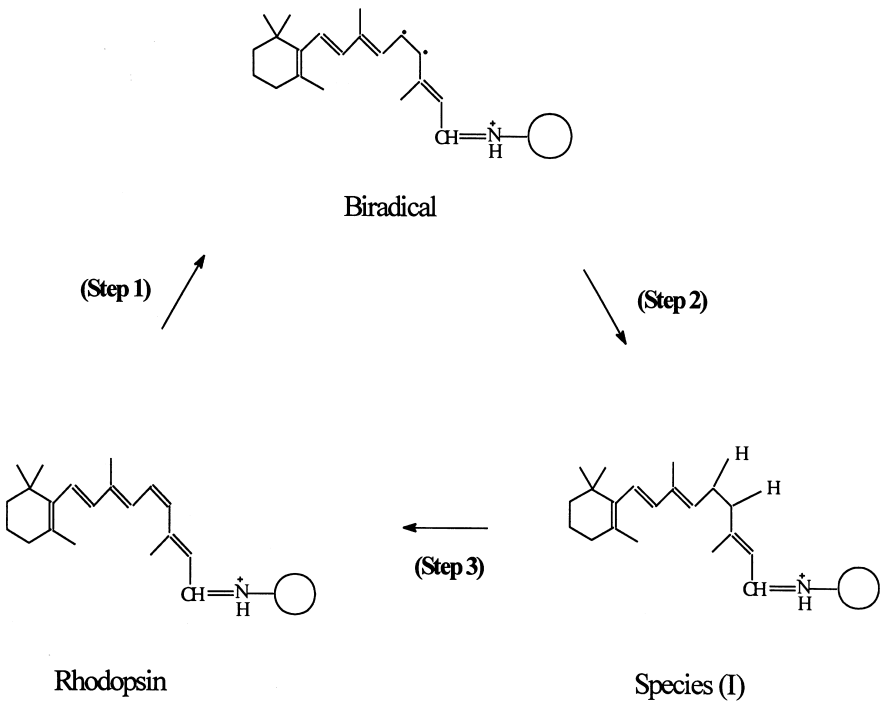

Fig. 2. The biradicals of vision chemistry.

drogen molecule, and releases an energy, equal to $\{DH^\circ$ (H–C, at 11) + DH° (H–C, at 12)$\}$, which results in a hydrogenated rhodopsin (I) (step 2). The dehydrogenation of species (I) gives rhodopsin and ends the thermochemical cycle (step 3).

According to the thermochemical cycle in Fig. 2, the π BDE can be expressed as:

$$\begin{aligned} DH^o(\mathrm{C, C{-}}\pi\mathrm{, at\ 11{-}12}) &= \{DH^o(\mathrm{H{-}C, at\ 11}) + DH^o(\mathrm{H{-}C, at\ 12}) \\ &\quad - DH^o(\mathrm{H{-}H})\} + \left\{\Delta_f H^o(\mathrm{I}) \right. \\ &\quad \left. - \Delta_f H^o(\mathrm{rhodopsin})\right\} \end{aligned} \quad (1)$$

Where (H–C, at 11) and DH° (H–C, at 12) are the H–C BDEs at the 11 and 12 positions, respectively; DH° (H–H) is the BDE of hydrogen molecules, i.e. 104.2 kcal/mol; $\Delta_f H^\circ$(rhodopsin) is the heat of formation of the rhodopsin complex; $\Delta_f H^\circ$(I) is the heat of formation of species (I). The heat of formation of neither rhodopsin nor species (I) is, of course, available and cannot be estimated. However, the difference of heats of formation between rhodopsin and species (I) can be estimated by Benson's group additivity rule [12,15].

Using the group language [12], the deference may be rewritten as:

$$\begin{aligned} \Delta\Delta_f H^o &= \Delta_f H^o(\mathrm{I}) - \Delta_f H^o(\mathrm{rhodopsin}) \\ &= \left\{\Delta_f H^o([\mathrm{C}_d - (\mathrm{C})(\mathrm{H})]) \right. \\ &\quad + 2\Delta_f H^o([\mathrm{C} - (\mathrm{C}_d)(\mathrm{C})(\mathrm{H})_2]) \\ &\quad \left. + \Delta_f H^o([\mathrm{C}_d - (\mathrm{C})_2])\right\} \\ &\quad - \left\{3\Delta_f H^o([\mathrm{C}_d - (\mathrm{C}_d)(\mathrm{H})]) \right. \\ &\quad \left. + \Delta_f H^o([\mathrm{C}_d - (\mathrm{C})(\mathrm{C}_d)])\right\} \end{aligned} \quad (2)$$

Where C_d represents a double-bonded carbon atom. Taking the updated group additivity values [15], we obtain.

$$\begin{aligned} \Delta\Delta_f H^o &= \Delta_f H^o(\mathrm{I}) - \Delta_f H^o\ (\mathrm{rhodopsin}) \\ &= \{8.55 + 2 \times (-4.8) + 10.19\} \end{aligned}$$

$$-\{3\times 6.78+8.76\}$$
$$=-19.96\ \text{kcal/mol}$$

An approach to predict the X–C BDEs has recently been developed [16–21], where X = hydrogen and halogen atoms, C-, Si-, Ge-, Sn-, N-, O- and S-centered groups. The H–C BDEs in unsaturated organic species can be estimated by the following equation:

$$DH^o(\text{H–C})_{\text{est}} = DH^o(\text{H–C(CH}_3)_m\text{H}_{3-m}) + \Delta V_{nb} + E_s \quad (3)$$

Where m is the degree of methyl substitution and $m = 1$, 2 or 3 for primary, secondary or tertiary carbon atom; DH° (H–C(CH$_3$)$_m$H$_{3-m}$) is the H–C BDEs of model compounds and is listed in [18] and it is 100.5, 97.0 and 94.1 kcal/mol, respectively; ΔV_{nb} is the steric compression relief resulting from the H–C bond cleavage and it may be negligible for the cases in Fig. 2. Because the H–C bonds at the 11 and 12 positions are secondary, so Eq. (3) becomes simpler:

$$DH^o(\text{H–C})_{\text{est}} = 97.0 + E_s\ \text{kcal/mol} \quad (4)$$

Where E_s is the resonance stabilization energy (RSE) of the polyenyl radicals. The RSEs of the following polyenyl radicals are known [22]:

$$E_s(\cdot\text{C–C=C}) = E_s(N=1) = -13.2\pm 1.0\ [20]\ \text{or}\ -13.5\ \text{kcal/mol}\ [22]$$

$$E_s(\cdot C\text{–C=C–C=C}) = E_s(N=2) = -17.5\pm 3\ [20]\ \text{or}\ -16.9\ \text{kcal/mol}\ [22]$$

$$E_s(\cdot C\text{–C=C–C=C–C=C}) = E_s(N=3) = -19.2\ \text{kcal/mol}\ [22]$$

Where N is the total number of the C–C–π bonds in the polyenyl radicals.

For the cleavage of the H–C bond at the 11 position in species (I), it gives an allylic radical. Based on Eq. (4), we have

$$DH^o(\text{H–C, at 12})_{\text{est}} = 97.0 - 13.2(\pm 1.0) = 83.8\pm 1.0\ \text{kcal/mol}$$

For the cleavage of the H–C bond at the 12 position in species (I), it gives a radical with $N = 3$. Thus, we have

$$DH^o(\text{H–C, at 11})_{\text{est}} = 97.0 - 19.2 = 77.8\pm 1\ \text{kcal/mol}$$

Substituting the values of DH° (H–C, at 11)$_{\text{est}}$, DH° (H–C, at 12)$_{\text{est}}$, DH° (H–H) and $\Delta\Delta_f H^\circ$ into Eq. (1), we obtain the estimated value of the C, C–π BDE:

$$DH^o(\text{C, } C\text{–}\pi\text{, at 11–12})_{\text{est}} = 37.4\pm 1.5\ \text{kcal/mol}$$

From physics, the conversion equation from kcal/mol to nm is given by

$$\lambda = \frac{N_A hc}{4.184\ DH^o} = \frac{28\,591.4}{DH^o}\,\text{nm} \quad (5)$$

Where N_A and h are the Avogadro and Planck's constant, respectively; c is the velocity of light. Thus, the energy of 37.4 ± 1.5 kcal/mol corresponds to the wavelength of 764 ± 30 nm. This wavelength is just the red limit observed by the naked eye [1–5].

3. On the violet limit

The violet limit of the wavelength of 380 nm is equivalent to 75.2 kcal/mol. This is a high energy that is enough to excite all π electrons, to induce π–π*, n–π* and n–σ* transitions and/or to break weakest H–C or C–C bonds in some species involved in the photo-induced *cis–trans* isomerization cycle which stops the cascade processes described in Fig. 1. As shown in a previous work [21], the H–C bond at position 15 of vitamin A is the weakest and is approximately 71.8 ± 2

kcal/mol. The C–C bond at position 1 and H–C bond at position 4 in vitamin A are also very weak. The respective BDEs are

$$DH^o(\text{C–C, at 1})_{\text{est}} = 73.6 \pm 2 \text{ kcal/mol}$$

$$DH^o(\text{H–C, at 4})_{\text{est}} = 75.8 \pm 2 \text{ kcal/mol}$$

Because the covalent force is short range, the $DH°$ (C–C, at 1) and $DH°$ (H–C, at 4) in *cis*- or *trans*-retinal, rhodopsin, bathorhodopsin and metarhodopsin can also be estimated to be 74 ± 2 and 76 ± 2 kcal/mol, respectively, almost the same as those in vitamin A.

It implies that the weakest bonds can be broken by absorption of a photon with a wavelength of 380 nm or less. As well known, the naked eye can be damaged by photons with a wavelength of 300 nm or more. The wavelength of 300 nm or less is equivalent to 95 kcal/mol or more. This energy is so much higher that it is enough to break almost all H–C, H–N, C, C–σ, C, O–σ, C, N–π and C, C–π bonds of organic species in the human eye and forming most of radicals or ions, which can further initiate many harmful chemical reactions harming health.

There are very interesting and complicated questions, such as, why can the light radiation cause the rhodopsin in the retina to bleach from red to white when we see? Why is infrared light sensitive to the eyes in some animals? The author feels that we need to further study the intramolecular energy-transfer, photochemistry of intermediates in the visual cycle and vision chemistry of animals to understand better such questions. Actually, the energy corresponding to the position of a maximum absorption peak of an organic species is always greater than the value of the π and/or σ BDEs. For example, the wavelength of a maximum absorption peak for ethene is 162 nm [23], but the C, C–π BDE of ethene molecule is 63.5–65 kcal/mol [9,10][1] (or 440–450 nm). This evident inconsistency will be discussed and explained in a separate paper [24], and it will be useful to determine which kinds of β-carotenes and polyenes have higher antioxidisability.

It should be emphasised that all of our estimates are from the information of gas-phase thermochemistry and kinetics. The solvent, temperature and other effects have not been considered. Even now, the knowledge available of thermochemistry and chemical kinetics in gas-phase is helpful in understanding important biochemical processes.

[1] Based on a cycle, similar to Fig. 2, the C, C–π BDE in ethene is given by:

$$\begin{aligned} DH^o(C,C-\pi)_{est} &= \{2DH^o(H-CH_2CH_3) \\ &\quad - DH^o(H-H)\} \\ &\quad + \{\Delta_f H^o(CH_3CH_3) \\ &\quad - \Delta_f H^o(CH_2CH_2)\} \\ &= \{2 \times 100.5(\pm 0.5) \\ &\quad - 104.2\} \\ &\quad + \{-20.0(\pm 0.1) \\ &\quad - 12.5(\pm 0.1)\} \\ &= 64.3 \pm 0.8 \text{ kcal/mol.} \end{aligned}$$

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