Corrections

Agonists and Partial Agonists of Rhodopsin: Retinals with Ring Modifications, by Reiner Vogel,* Friedrich Siebert, Steffen Lüdeke, Amiram Hirshfeld, and Mordechai Sheves*, Volume 44, Number 35, September 6, 2005, pages 11684−11699.

There is an error in the calculation of the enthalpy change ΔH and the entropy change ΔS of the Meta I−Meta II equilibrium in the Supporting Information due to incorrect use of the Henderson−Hasselbalch equation. Correctly, the equation is

$$pK = pH + \log_{10} \frac{[MII]}{[MI]} = \log_{10} \frac{[MII]}{[MI][H^+]} = \log_{10} K_{eq}$$

which yields $K_{eq} = 10^{pK}$, and therefore

$$\ln K_{eq} = (\ln 10)pK \tag{4}$$

Inserting this expression into eq 3 of the Supporting Information yields the following expression for ΔH (with $\ln 10 \approx 2.303$)

$$\Delta H = -R \times 2.303 \frac{pK_2 - pK_1}{\dfrac{1}{T_2} - \dfrac{1}{T_1}} =$$

$$R \times 2.303(pK_1 - pK_2)\frac{T_1 T_2}{T_1 - T_2} \tag{5}$$

which is not affected by the error.

Evaluating eq 2 at T_2 and insertion of eqs 4 and 5 yield the following expression for the change of entropy of the transition

$$\Delta S = R \ln K_{eq} + \frac{\Delta H}{T} =$$

$$R \times 2.303\left[pK_2 + (pK_1 - pK_2)\frac{T_1 T_2}{(T_1 - T_2)T_2}\right]$$

This can be simplified to

$$\Delta S = R \times 2.303\left(\frac{pK_1 T_1 - pK_2 T_2}{T_1 - T_2}\right) \tag{6}$$

which is independent of pH.

The values for ΔS stated in Table 1 in the paper are therefore shifted uniformly and by 134 J mol^{-1} K^{-1} too low. The corrected version of Table 1 is given.

Table 1: Enthalpy and Entropy Changes in the Meta I−Meta II Equilibria of Selected Pigments[a]

	pK_a at 20 °C	pK_a at 0 °C	ΔpK_a	ΔH (kJ/mol)	ΔS (J mol^{-1} K^{-1})	$T\Delta S$ at 20 °C (kJ/mol)
native	7.7	6.6	1.1	84	434	127
acyclic-1	4.8	4.0	0.8	61	301	88
acyclic-2	5.0	4.1	0.9	69	331	97
16,17-demethyl	5.8	4.8	1.0	77	372	109
16,17,18-demethyl	5.2	4.5	0.7	54	282	83
opsin[b]	−	−	−	48	236	69

[a] ΔpK_a is the difference between the pK_a values measured at 0 and 20 °C. The estimated error margins for ΔH and ΔS are 15 kJ/mol and 54 J mol^{-1} K^{-1}, respectively. [b] Opsin conformational equilibrium; see the text for details.

The experimental values for the thermodynamic parameters of the Meta I−Meta II equilibrium of the native pigment at 20 °C are 84 kJ/mol for ΔH, 127 kJ mol^{-1} for $T\Delta S$, and thus −43 kJ/mol for ΔG.

The absolute shift of the ΔS values by 134 J mol^{-1} K^{-1} affects the synthetic pigments in the same way as the native pigment. Our conclusions regarding the single pigments are based on changes in ΔS and are therefore not affected by the error.