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Research

Comparison of Thermal Performance Equations in Describing Temperature-Dependent Developmental Rates of Insects: (II) Two Thermodynamic Models

Pei-Jian Shi,[1,2] Gadi V. P. Reddy,[3,4] Lei Chen,[5] and Feng Ge[2]

[1]Co-Innovation Centre for Sustainable Forestry in Southern China, Bamboo Research Institute, Nanjing Forestry University, Nanjing 210037, China (peijianshi@gmail.com), [2]State Key Laboratory of Integrated Management of Pest Insects and Rodents, Institute of Zoology, Chinese Academy of Sciences, Beijing 100101, China (gef@ioz.ac.cn), [3]Montana State University, Western Triangle Ag Research Center, 9546 Old Shelby Rd, P. O. Box 656, Conrad, MT 59425 (reddy@montana.edu), [4]Corresponding author, e-mail: reddy@montana.edu and [5]Graduate School of Environmental Science, Hokkaido University, N19W8, Sapporo 060-0819, Japan (lei-chen1029@eis.hokudai.ac.jp)

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Abstract

There are many descriptive statistical models describing the temperature-dependent developmental rates of insects without derivation of biophysical processes; thus, it is difficult to explain how temperature affects development from the thermodynamic mechanisms. Fortunately, two mathematical models (the Sharpe–Schoolfield–Ikemoto [SSI] model and Ratkowsky–Olley–Ross [ROR] model) based on thermodynamics have been built to explain temperature-dependent reaction rates. Despite their differences in construction, both models produce similar functions when used to describe the effect of temperature on the probability of a theoretical rate-controlling enzyme that is in its active state. However, the previous fitting method of the SSI model was unable to achieve global optimization of parameter estimates; that of the ROR model usually underestimates the maximal probability of the rate-controlling enzyme that is in its active state, as found in some empirical data sets. In the present study we improved the fitting methods for these two models. We then used these two models to fit 10 data sets from published references. We found the models based on the improved fitting methods agree with the empirical data well and predict that the maximal probabilities of the rate-controlling enzyme that is in its active state are close to 1. The SSI model produces a slightly better goodness-of-fit value for the model than the ROR model, whereas the latter predicts a more symmetrical curve for the probability of the rate-controlling enzyme that is in its active state. If thermodynamic parameters of two or more different species are to be compared, we recommend that researchers use one or the other of these two models and follow the same fitting methods for all species.

Key words: differential evolution, intrinsic optimum temperature, optimization, quartic polynomial, residual sum of squares

The thermal performance curves of ecotherms are nonlinear and highly asymmetrical, and the temperature that corresponds with maximal performance is usually right skewed (Martin and Huey 2008). Typical performance curves of insects include the developmental rates, intrinsic rates of increase, and net reproductive rates at various constant temperatures. The developmental rate is the reciprocal of developmental time required to complete a certain developmental stage at a given temperature, which is used to measure the developmental speed over a period at a temperature (Uvarov 1931, Campbell et al. 1974). The intrinsic rate of increase and net reproductive rate of a study species come from the calculation of life table parameters, which are usually employed to reflect the fitness of insects (Huey and Berrigan 2001). The intrinsic rate of increase is equivalent to the instantaneous rate of increase in an exponential growth of population (Shi et al. 2012, 2013). These three biological measures have similarly shaped curves, but the temperatures in data sets that correspond to the curves' inflection point (usually referred to as the "optimum" temperature), are usually different across the three measures (Huey and Berrigan 2001). The "optimum" temperature for the net reproductive rate is usually lower than that for the species' intrinsic rate of increase. Evidence demonstrates the effects of temperature on the intrinsic rate of increase and the net reproductive rate of insects can be expressed by the same mathematical equation as that describing the temperature-dependent developmental rate of insects (Martin and Huey 2008, Shi et al. 2012). Thus, conclusions from model comparison for the thermal developmental rate of insects will also apply to the intrinsic rate of increase and the net reproductive rate of insects. In this study we did not investigate models for either the intrinsic rate of increase or the net reproductive rate, instead we focused only on the developmental rate. It is an extension of our previous study in Shi et al. (2016) when our interest was to compare different developmental rate models.

There are many mathematical models that have been used to describe the temperature-dependent developmental rates of bacteria and ectotherms (Logan et al. 1976, Sharpe and DeMichele 1977, Schoolfield et al. 1981, Taylor 1981, Wang et al. 1982, Ratkowsky et al. 1983, Rosso et al. 1993, Lactin et al. 1995, Yin et al. 1995, Brière et al. 1999, Ratkowsky et al. 2005, Ikemoto 2008, Shi et al. 2011, Corkrey et al. 2012, Régnière et al. 2012, Ikemoto et al. 2013, also see Wagner et al. 1984 and references therein). These models can be divided into two categories: 1) purely descriptive statistical models and 2) theoretical thermodynamic models. Our recent study (see Shi et al. 2016) compared some descriptive models and found the model proposed by Ratkowsky et al. (1983) to be better than the others while using 10 data sets describing the temperature-dependent developmental rates of insects. However, Ratkowsky demonstrated that the model proposed by Rosso et al. (1993), which was overlooked by Shi et al. (2016), could be even better than the Ratkowsky model (personal communication with Prof. David A. Ratkowsky). Although the descriptive model has high flexibility for fitting observations, it lacks thermodynamic information among model parameters. That is, any purely descriptive statistical model lacks the basis of bio-physics, which is only used to simulate the curve tendency at different temperatures without knowing the inner mechanisms. In contrast to descriptive statistical models, two thermodynamics-based mathematical models have clear bio-physical meanings identified during the equation-derivation processes: 1) the SSI model proposed by Sharpe and DeMichele (1977) and modified by Schoolfield et al. (1981) and Ikemoto (2008), and 2) the second, or ROR model, proposed by Ratkowsky et al. (2005) and Corkrey et al. (2012). These two thermodynamic models both predict a similar probability curve of a developmental rate-controlling enzyme being in its native state, where there is an "optimum" temperature corresponding to the maximum probability of the enzyme being in its native state. There is a difference in the predicted curve probability between these two models. The SSI model usually provides an asymmetrical but approximately bell-shaped probability curve, while the ROR model predicts a perfectly symmetrical probability curve. Although these two models can both fit the developmental rate of insects well, few entomologists have paid attention to these two models, probably because each has many parameters and complicated structures. For example, two models proposed by Brière et al. (1999) are frequently used by entomologists because they are simple, having just three and four parameters, respectively. Meanwhile, the SSI model has six parameters and the ROR model has eight. Too many parameters make data fitting unstable and slow to converge, which is another reason why the SSI and ROR models have been largely neglected in entomological research. In addition, there are no relevant studies systematically comparing these two thermodynamic models. In the present study, we attempted to provide new methods for fitting the SSI and ROR models, and to compare them using 10 data sets of temperature-dependent developmental rates of insects collected in Shi et al. (2016).

Materials and Methods

Data

We used 10 data sets of the temperature-dependent developmental rates of insects and mites (see Table 1 for detail). The data sets are the same as those in Shi et al. (2016).

Models

Arrhenius (1889) put forward an empirical equation to describe the effect of temperature on the rate constant of a chemical reaction:

$$r(T) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where $r(T)$ is the rate constant of a chemical reaction (time unit^{-1}) at absolute temperature T, A is a pre-exponential factor (time unit^{-1}), E_a is the activation free energy (cal·mol^{-1}), and R is the universal gas constant (1.987 cal·mol^{-1}·deg^{-1}). The rate constant of the chemical reaction is usually directly used as the developmental rate of plants and poikilotherms (e.g., Aono and Kazui 2008). Erying (1935) built a similar exponential equation based on the absolute chemical reaction-rate theory:

$$r(T) = \frac{\kappa K T}{\mathrm{h}} \cdot \exp\left(\frac{\Delta S^{\ddagger} - \Delta H^{\ddagger}/T}{R}\right) = B \cdot T \cdot \exp\left(-\frac{\Delta H_A^{\ddagger}}{RT}\right) \quad (2)$$

where a) κ is a transmission coefficient (without units), b) K is Boltzman's constant (cal·molecule^{-1}·deg^{-1}), c) h is Planck's constant (cal·s), a physical constant that is the quantum of action, central in quantum mechanics, d) $\Delta S^{\ddagger}$ is the entropy of activation (cal·mol^{-1}·deg^{-1}), e) B is a pre-exponential factor, and f) $\Delta H_A^{\ddagger}$ is the enthalpy of activation of the reaction that is catalyzed by the enzyme (cal·mol^{-1}).

Table 1. Ten data sets of temperature-dependent developmental rates of insects and mites

Data set	Species	Order: Family	Stage	Thermal range (°C)	Sample size	Source
1	*Helicoverpa armigera* Hübner	Lepidoptera: Noctuidae	Pupa	15.0–37.0	23	Wu et al. (2009)
2	*Kampimodromus aberrans* Oudemans	Acari: Phytoseiidae	Egg+larva+1st–2nd nymph	15.0–35.0	9	Broufas et al. (2007)
3	*Toxorhynchites brevipalpis* Theobald	Diptera: Culicidae	Egg	14.0–32.0	19	Trpis (1972)
4	*Bactrocera dorsalis* Hendel	Diptera: Tephritidae	Egg	12.5–36.5	19	Messenger and Flitters (1958)
5	*Aedes aegypti* L.	Diptera: Culicidae	Larva	15.5–35.0	15	Gilpin and McClelland (1979)
6	*Bemisia tabaci* (B-biotype) Gennadius	Hemiptera: Aleyrodidae	From egg to adult	18.0–36.0	7	Xiang et al. (2007)
7	*Lipaphis erysimi* Kaltenbach	Hemiptera: Aphididae	From egg to adult	8.3–35.1	12	Liu and Meng (2000)
8	*Myzus persicae* Sulzer	Hemiptera: Aphididae	From egg to adult	6.2–30.0	11	Liu and Meng (1999)
9	*Epilachna varivestis* Mulsant	Coleoptera: Coccinellidae	Larva	12.5–32.5	8	Shirai and Yara (2001)
10	*Drosophila buzzatii* Patterson & Wheeler	Diptera: Drosophilidae	From egg to adult	15.1–31.8	9	de Jong (2010)

The Eyring equation actually assumes no control enzyme inactivation. Sharpe and DeMichele (1977) assumed that the control enzyme can exist in two temperature-dependent inactivation states as well as an active state, and based on the reaction kinetics of development the authors of these papers proposed a new nonlinear developmental rate model under nonlimiting substrate conditions:

$$r(T) = T \cdot \exp\left(\frac{\varphi - \Delta H_A^{\ddagger}/T}{R}\right) \cdot P_2(T) \tag{3}$$

where φ is a conversion factor with no thermodynamics meaning ($^{\circ}K^{-1}\cdot s^{-1}$), and $P_2(T)$ is the probability of rate-controlling enzyme being its native state:

$$P_2(T) = \frac{1}{1 + \exp\left(\frac{\Delta S_L - \Delta H_L/T}{R}\right) + \exp\left(\frac{\Delta S_H - \Delta H_H/T}{R}\right)} \tag{4}$$

in which ΔS_L is the change in entropy associated with low temperature inactivation of the enzyme ($cal\cdot deg^{-1}\cdot mol^{-1}$), ΔH_L is the change in enthalpy associated with low temperature inactivation of the enzyme ($cal\cdot mol^{-1}$), ΔS_H is the change in entropy associated with high temperature inactivation of the enzyme ($cal\cdot deg^{-1}\cdot mol^{-1}$), and ΔH_H is the change in enthalpy associated with high temperature inactivation of the enzyme ($cal\cdot mol^{-1}$).

Schoolfield et al. (1981) improved the model proposed by Sharpe and DeMichele (1977) by introducing the parameter of $\rho_{(25^{\circ}C)}$, which was defined as follows:

$$\rho_{(25^{\circ}C)} = 298.15 \cdot \exp\left(\frac{\varphi - \Delta H_A^{\ddagger}/298.15}{R}\right) \tag{5}$$

If we let $T_{1/2L}$ denote the temperature ($^{\circ}K$) at which the enzyme is 1/2 active and 1/2 low temperature inactive, and let $T_{1/2H}$ denote the temperature ($^{\circ}K$) at which the enzyme is 1/2 active and 1/2 high temperature inactive and these are expressed as:

$$\begin{cases} T_{1/2L} = \dfrac{\Delta H_L}{\Delta S_L} \\ T_{1/2H} = \dfrac{\Delta H_H}{\Delta S_H} \end{cases} \tag{6}$$

Then Schoolfield et al. (1981) developed the following mathematical expression:

$$\begin{aligned} r(T) &= P_2(T) \cdot \rho_{(25^{\circ}C)} \cdot \frac{T}{298.15} \cdot \exp\left[\frac{\Delta H_A^{\ddagger}}{R} \cdot \left(\frac{1}{298.15} - \frac{1}{T}\right)\right] \\ &= \frac{\rho_{(25^{\circ}C)} \cdot \frac{T}{298.15} \cdot \exp\left[\frac{\Delta H_A^{\ddagger}}{R} \cdot \left(\frac{1}{298.15} - \frac{1}{T}\right)\right]}{1 + \exp\left[\frac{\Delta H_L}{R} \cdot \left(\frac{1}{T_{1/2L}} - \frac{1}{T}\right)\right] + \exp\left[\frac{\Delta H_H}{R} \cdot \left(\frac{1}{T_{1/2H}} - \frac{1}{T}\right)\right]} \end{aligned} \tag{7}$$

This revised version has an important assumption that at 25 °C the rate-controlling enzyme is in its native state (namely P_2) and reaches its maximum, which is defined as the most suitable temperature for ectothermal survival. However, 25 °C, as an ideal temperature, does not apply to all ectotherms as the point where P_2(T) is maximized (Ikemoto 2005, 2008, de Jong 2010, Shi et al. 2013). Ikemoto (2005) proposed relaxing the limit of 25 °C to a variable (T_{Φ}) that could be different for different species:

$$r(T) = P_2(T) \cdot \rho_{\Phi} \cdot \frac{T}{T_{\Phi}} \cdot \exp\left[\frac{\Delta H_A^{\ddagger}}{R} \cdot \left(\frac{1}{T_{\Phi}} - \frac{1}{T}\right)\right] \tag{8}$$

ρ_{Φ} represents the developmental rate at T_{Φ} without considering the inactivation of the theoretical rate-controlling enzyme, i.e., P_2 is hypothesized to be ~1. The other parameters are the same as those in the model proposed by Schoolfield et al. (1981). By using the condition $dP_2/dT = 0$, Ikemoto (2005) derived equation (9) as:

$$T_{\Phi} = \frac{\Delta H_L - \Delta H_H}{R \cdot \ln\left(-\frac{\Delta H_L}{\Delta H_H}\right) + \frac{\Delta H_L}{T_{1/2L}} - \frac{\Delta H_H}{T_{1/2H}}} \tag{9}$$

We refer to equation (8) as the SSI model. To reduce the number of model parameters, for easy data fitting, Ikemoto (2008) recommended that $T_{1/2L}$ and $\Delta H_A^{\ddagger}$ be pre-determined via linear fitting, and at the same time to limit the parameter of ρ_{Φ} on the straight line in the mid-temperature range. $T_{1/2L}$ (transferred to °C) equals the lower developmental threshold, expressed in absolute temperature; $\Delta H_A^{\ddagger}$ equals $-R\cdot\beta$ where β is the slope of straight line in the mid-temperature range on the Arrhenius' plot ($\ln[r]$ versus the reciprocal of absolute temperature). In this case, the predicted maximum value for P_2 will not deviate much from 1 because ρ_{Φ} is limited on the straight line on the plot of r versus temperature that can approximate the SSI model curve in the mid-temperature range. Ikemoto et al. (2013) provided an option that $T_{1/2L}$ can be recalculated by optimization methods, such as the Nelder–Mead algorithm (Nelder and Mead 1965), to enhance the goodness of fit.

Interestingly, Johnson and Lewin (1946) proposed a new thermodynamic model also based on the Eyring equation but with different model hypotheses:

$$r(T) = \frac{c \cdot T \cdot \exp\left(-\Delta H_A^{\ddagger}/RT\right)}{1 + \exp\left(\frac{\Delta S - \Delta H/T}{R}\right)} \tag{10}$$

Here, c is a pre-exponential factor, ΔH is the difference in enthalpy between the catalytically active and inactive states of the enzyme system, and ΔS is the difference in entropy between these two states. Ratkowsky et al. (2005) introduced the Gibbs free energy change (ΔG), which equals:

$$\Delta G = \Delta H - T \cdot \Delta S \tag{11}$$

Then the Johnson–Lewin equation can be re-written as:

$$r(T) = \frac{c \cdot T \cdot \exp\left(-\Delta H_A^{\ddagger}/RT\right)}{1 + \exp(-\Delta G/RT)} \tag{12}$$

and ΔG can be reformulated as follows (Ratkowsky et al. 2005):

$$\Delta G = \Delta H^* - T \cdot \Delta S^* + \Delta C_p \cdot \left[\left(T - T_H^*\right) - T \cdot \ln\left(T/T_S^*\right)\right] \tag{13}$$

where a) ΔH^* is the enthalpy change at T_H, the convergence temperature for enthalpy, b) ΔS^* is the entropy change at T_S^*, the convergence temperature for entropy, and c) ΔC_p is the heat capacity change between the native and denatured stated of the key enzyme systems. Let n be the number of amino acid residues in the protein. Substituting equation (13) for ΔG in equation (12), Ratkowsky et al. (2005) obtained the new thermodynamics equation:

$$r(T) = \frac{c \cdot T \cdot \exp\left(-\Delta H_A^{\ddagger}/RT\right)}{1 + \exp(-n\{\Delta H^* - T \cdot \Delta S^* + \Delta C_p \cdot [(T - T_H^*) - T \cdot \ln(T/T_S^*)]\}/RT)} \tag{14}$$

Let $c = \exp(b)$, then we can get:

$$r(T) = \frac{T \cdot \exp\left(b - \Delta H_A^{\ddagger}/RT\right)}{1 + \exp(-n\{\Delta H^* - T \cdot \Delta S^* + \Delta C_p \cdot [(T - T_H^*) - T \cdot \ln(T/T_S^*)]\}/RT)} \tag{15}$$

We refer to equation (15) as the ROR model. The reciprocal of the denominator also represents the probability of rate-controlling

enzyme being in its native state, which has the same meaning with P_2 in the SSI model. In the SSI model, T_Φ represents the temperature that maximizes the value of P_2. In the ROR model, there is an equivalent temperature (T_{mes}) that maximizes P_2, which can be further expressed as:

$$T_{mes} = T_H^* - \Delta H^*/\Delta C_p \tag{16}$$

There are eight parameters in the ROR model. Ratkowsky et al. (2005) proposed to fix three parameters as constants: T_H^*=373.6 K, T_S^*=385.2 K, and ΔS^*=18.1 J·K^{-1} (mol amino acid residue). Values given in joules by the model can be transferred to calories in the ROR model system. We fused joules in the ROR model for easy comparison with the former parameters in Ratkowsky et al. (2005) and Corkrey et al. (2012). In addition, R in the ROR model is expressed as 8.314 J·K^{-1}·mol^{-1}.

The previous method of fitting the SSI model requires users to provide the data range for performing the linear fitting, which is used to calculate the lower developmental threshold (i.e., $T_{1/2L}$ whose unit is transferred to °C) and the enthalpy of activation of the reaction that is catalyzed by the enzyme (i.e., $\Delta H_A^\ddagger$). However, we feel that it is subjective to use the investigators' experience to predetermine the linear range. In addition, the previous fitting method cannot obtain the global optimization solution because the results from using the "optim" function (see Ikemoto et al. 2013 in detail) is only a local optimization solution, which relies on the chosen initial values of parameters. The previous fitting method of the ROR model sometimes predicts the unreasonable probabilities of rate-controlling enzyme being in its native state because the maximum probability is probably very much less than 1 (see Fig. 1 published in Ratkowsky et al. 2005).

New Fitting Methods for Two Thermodynamics Models

For the SSI model, we used another expression of equation (9) as follows:

$$T_{1/2H} = \frac{\Delta H_H}{R \cdot \ln\left(-\frac{\Delta H_L}{\Delta H_H}\right) + \frac{\Delta H_L}{T_{1/2L}} + \frac{\Delta H_H - \Delta H_L}{T_\Phi}} \tag{17}$$

Then we substituted equation (17) into equation (8) and built a nonlinear relationship between ρ_Φ and T_Φ. In the previous fitting method, there is a straight linear relationship between them. However, the linear range of data must be predetermined by users. To reduce the subjectivity of choosing the linear range, we used the quartic polynomial to fit the temperature-dependent developmental rates related to the SSI model:

$$\begin{aligned} r(T_\Phi) &= \rho_\Phi \\ &= \alpha_0 + \alpha_1(T_\Phi - 273.15) + \alpha_2(T_\Phi - 273.15)^2 \\ &\quad + \alpha_3(T_\Phi - 273.15)^3 + \alpha_4(T_\Phi - 273.15)^4 \end{aligned} \tag{18}$$

α_j (j ranges 0 to 4) are regression coefficients. In this case, the SSI model has now only five parameters. The differential evolution (Price et al. 2005, Storn and Price 1997) was used to estimate the parameters of the SSI model. We also used the quartic polynomial to fit the temperature-dependent developmental rates related to the ROR model:

$$\begin{aligned} r(T_{mes}) &= T_{mes} \cdot \exp\left(b - \Delta H_A^\ddagger / R T_{mes}\right) \\ &= \alpha_0 + \alpha_1(T_{mes} - 273.15) + \alpha_2(T_{mes} - 273.15)^2 \\ &\quad + \alpha_3(T_{mes} - 273.15)^3 + \alpha_4(T_{mes} - 273.15)^4 \end{aligned} \tag{19}$$

Then we have:

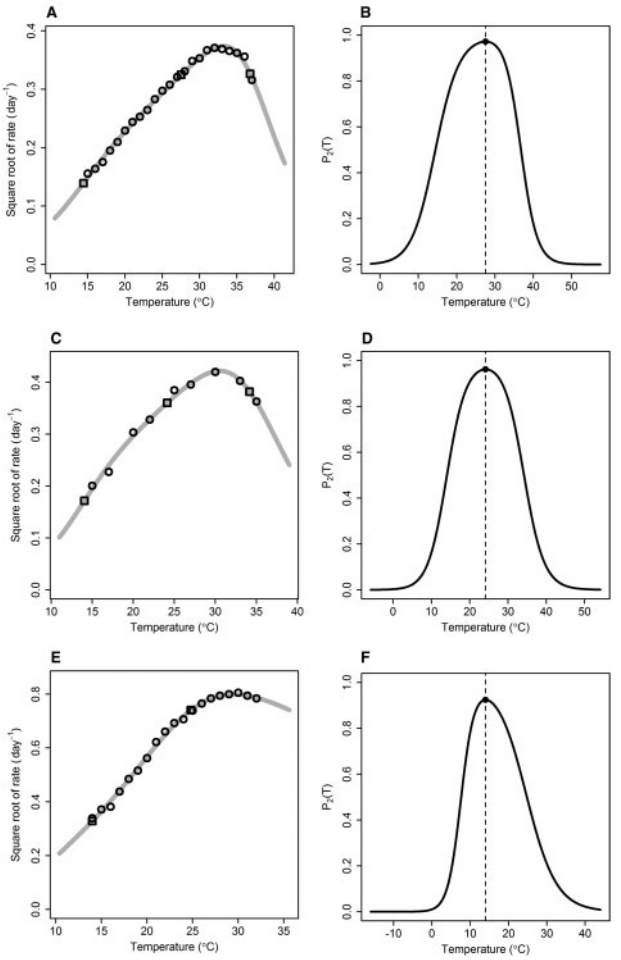

Fig. 1. Fitted the square roots of developmental rates and the predicted probability of rate-controlling enzyme being in its native state using the SSI model. (**A**, **B**) *Helicoverpa armigera*; (**C**, **D**) *Kampimodromus aberrans*; (**E**, **F**) *Toxorhynchites brevipalpis*. The small open circles represent the square roots of observed developmental rates; three small open squares represent the development rates at $T_{1/2L}$, T_Φ, and $T_{1/2H}$; and the gray curve represents the predicted square roots of developmental rates.

$$b = \ln\left(\frac{r(T_{mes})}{T_{mes}}\right) + \frac{\Delta H_A^\ddagger}{R \cdot T_{mes}} \tag{20}$$

We next relax T_H^* to be an unknown parameter to enhance the model fitting flexibility. We also tried relaxing T_S^* and ΔS^* to be unknown model parameters, but changing these two parameters did not improve the goodness of fit larger than only changing T_H^*. Thus, we still keep T_S^*=385.2 K and ΔS^*=18.1 J·K^{-1} following Ratkowsky et al. (2005). Therefore, the revised ROR model still had five parameters. We also used the differential evolution method (Price et al. 2005) to fit the ROR model. A transformation is required when the variance is not homogeneous. In general, directly fitting the developmental rates as the response variable will lead to the heterogeneity of variance (personal communication with Prof. David A. Ratkowsky). Thus, it is better to use the square root transformation for the temperature-dependent developmental rate data (Ratkowsky 1990).

Because the SSI and ROR models both have five parameters, it is unnecessary to use more complex indicators such as the Akaike information criterion (AIC) and adjusted coefficient of determination to compare them. In the present study, we used the residual sum of

squared (RSS) and coefficient of determination (R^2). We also provided the root mean squared errors (RMSE) and chi square (χ^2).

$$\mathrm{RSS}=\sum_{i=1}^{q}\left(\sqrt{r_i}-\widehat{\sqrt{r_i}}\right)^2 \quad (21)$$

$$\mathrm{RMSE}=\sqrt{\frac{\sum_{i=1}^{q}\left(\sqrt{r_i}-\widehat{\sqrt{r_i}}\right)^2}{q}} \quad (22)$$

$$\chi^2=\sum_{i=1}^{q}\frac{\left(\sqrt{r_i}-\widehat{\sqrt{r_i}}\right)^2}{\widehat{\sqrt{r_i}}} \quad (23)$$

Here, q represents the sample size, and the hat symbol over a parameter, represents the predicted value.

The statistical software R (version 3.2.2; R Core Team 2015) was used to fit the data and draw the figures. The special R package of "DEoptim" was used to carry out the optimization. Three R functions were developed based on the "DEoptim" function and the "optim" function to fit the SSI, early five-parameter ROR, and the revised five-parameter ROR models (see Supp. Material 1 [online only] in detail).

Results

The fitted results using the SSI model are listed in Table 2. Fig. 1 shows the comparison between the observed and predicted square roots of temperature-dependent developmental rates and the predicted probability of rate-controlling enzyme being in its native state from data set 1 to data set 3. We did not show the other data sets again, and the fitted parameters and the goodness of fit of the remaining data sets can be found in Table 2. The observations are well reflected by the SSI model. The predicted probability curve of rate-controlling enzyme being in its native state is approximately bell-shaped around T_Φ. However, the left and right portions are not perfectly symmetrical.

Table 3 shows the fitted results using the early five-parameter ROR model (Ratkowsky et al. 2005). Meanwhile, Fig. 2 shows the comparison between the observed and predicted square roots of temperature-dependent developmental rates and the predicted probability of rate-controlling enzyme being in its native state from data set 1 to data set 3. We found that the predicted maximum probability of rate-controlling enzyme being in its native state to be too small for data set 3 in that it was even less than 0.1. This contradicts the definition of the probability. The data were probably overfitted, resulting in the incorrect estimates of the parameters by the ROR model. Use of the revised five-parameter ROR model improved the predicted probability of the rate-controlling enzyme being in its native state and make the maximum probability at T_{mes} approximate to 1 (see Fig. 3; also exhibiting the comparison between the observed and predicted square roots of developmental rates). In addition, the predicted probability curve of the ROR model was perfectly symmetrical around T_{mes}. However, the revised five-parameter ROR model had lower goodness of fit than the SSI model (Tables 2 and 4). Except from data sets 2 and 7, the coefficients of determination for the majority of data sets using the revised ROR model were still more than 0.99, demonstrating that the revised five-parameter ROR model can still reflect the effect of temperature on the developmental rates well.

Discussion

Although the SSI and ROR models are both based on the thermodynamic theory, and both date back to the Eyring equation (Eyring 1935), the estimates of thermodynamic parameters in these two models are too sensitive to the fitting methods. A small change in one parameter can result in large changes to other parameter estimates, making it problematic to provide a reliable estimate of a thermodynamic parameter. There is an important parameter, $T_{\Phi,}$ in the SSI model and one, $T_{mes,}$ in the ROR model, both of which are the temperature with the greatest probability of the enzyme being in its native state (referred to as the intrinsic optimum temperature). However, the early five-parameter ROR model, the revised five-parameter ROR model, and the SSI model did not make the same estimate for this temperature. Even the two ROR models made estimates differing by more than 2 °C for T_{mes} across several data sets used in the present study. There was an 8.7 °C difference in the intrinsic optimum temperature between the revised ROR model and the SSI model for data set 3, and a difference of 7.3 °C for data set 6. Ratkowsky et al. (2005) proposed to fix three thermodynamic constants: T_H^*=373.6, T_S^*=385.2, and ΔS^*=18.1 during fitting of the model. This early version of the ROR model can fit the data of the temperature-dependent growth rates of bacteria, the temperature-dependent developmental rates, and their square roots very well. If we change the values for the above three constants, it will affect the final estimates of other parameters. In this case, the estimated thermodynamic parameters actually cannot accurately reflect the actual values that can measured in the bio-physical experiments. These results are only theoretical values related to a particular model system (including the same parameters and predetermined fitting method). Thus, it is necessary to follow a fixed model system for comparing

Table 2. Parameter estimate and goodness of fit using the SSI model

Parameter	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5	Data set 6	Data set 7	Data set 8	Data set 9	Data set 10
T_Φ	300.7	297.3	287.2	304.5	293.3	301.6	295.3	291.8	289.7	292.4
ΔH_L	−52609.9	−65211.2	−90382.6	−46558.0	−123232.3	−43960.5	−50849.4	−54549.1	−183777.0	−90015.4
ΔH_H	91272.9	71773.9	45917.1	177015.8	62803.1	129406.0	59704.4	70169.1	60186.6	63657.5
$T_{1/2L}$	287.6	287.2	280.8	290.4	286.2	285.6	283.0	279.1	284.3	284.3
$\Delta H_A^\ddagger$	12917.7	13339.6	34709.9	7090.8	22048.3	8756.2	11012.7	13657.6	17160.7	22336.8
ρ_Φ	0.108	0.135	0.117	1.000	0.102	0.063	0.156	0.125	0.022	0.050
$T_{1/2H}$	309.9	307.3	298.0	309.9	306.2	309.0	307.2	303.3	304.0	303.8
RSS	0.000413	0.000401	0.001325	0.002000	0.000409	0.000027	0.000477	0.000203	0.000010	0.000148
RMSE	0.004238	0.006679	0.008352	0.010261	0.005222	0.001962	0.006302	0.004294	0.001099	0.004049
χ^2	0.001559	0.001421	0.002709	0.003768	0.001170	0.000132	0.001458	0.000613	0.000050	0.000625
R^2	0.9964	0.9919	0.9973	0.9983	0.9972	0.9961	0.9956	0.9981	0.9992	0.9965

RSS represents the residual sum of squared; RMSE represents the root mean squared error; χ^2 represents the chi-square; and R^2 represents the coefficient of determination.

Table 3. Parameter estimate and goodness of fit using the early five-parameter ROR model

Parameter	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5	Data set 6	Data set 7	Data set 8	Data set 9	Data set 10
T_{mes}	297.4	295.9	297.9	297.5	295.8	297.2	293.8	290.2	294.0	293.2
ΔH^*	5344.8	5336.3	5089.8	5345.2	5342.6	5345.9	5337.3	5344.1	5344.3	5337.7
n	330.4	252.5	158.0	422.1	306.5	591.3	179.5	281.2	464.5	267.0
$\Delta H_A^{\ddagger}$	68290.7	67161.9	49449.6	62696.2	83284.9	47260.4	54221.4	63261.3	59553.3	92636.6
b	19.57	19.99	29.23	19.27	26.47	10.42	15.08	18.51	15.37	29.87
ΔC_p	70.10	68.71	67.26	70.27	68.71	70.01	66.86	64.10	67.11	66.40
RSS	0.000370	0.000284	0.001604	0.004173	0.000365	0.000028	0.000270	0.000170	0.000011	0.000108
RMSE	0.004013	0.005615	0.009188	0.014819	0.004930	0.001999	0.004743	0.003926	0.001193	0.003463
χ^2	0.001412	0.000994	0.003627	0.005545	0.001001	0.000131	0.000799	0.000519	0.000057	0.000480
R^2	0.9968	0.9943	0.9967	0.9965	0.9975	0.9959	0.9975	0.9984	0.9991	0.9974

$T_H^* = 373.6$ K, $T_S^* = 385.2$ K, and $\Delta S^* = 18.1$ J·K^{-1}. ΔC_p is calculated by equation (16).

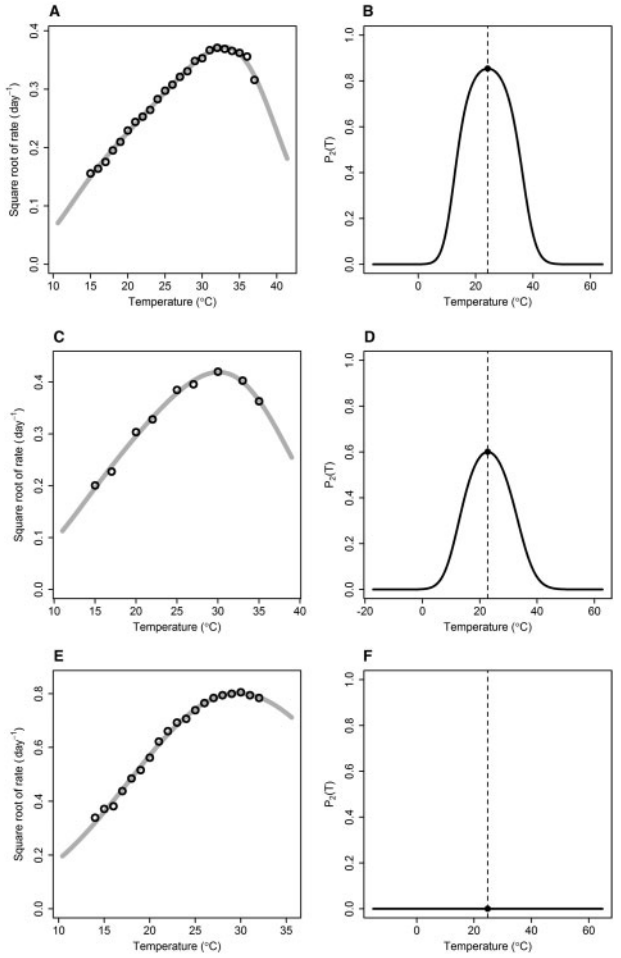

Fig. 2. Fitted square roots of developmental rates and the predicted probability of rate-controlling enzyme being in its native state using the early ROR model (Ratkowsky et al. 2005). The species names in six panels are the same as those in Fig. 1. The small open circles represent the square roots of observed developmental rates; and the gray curve represents the predicted square roots of developmental rates.

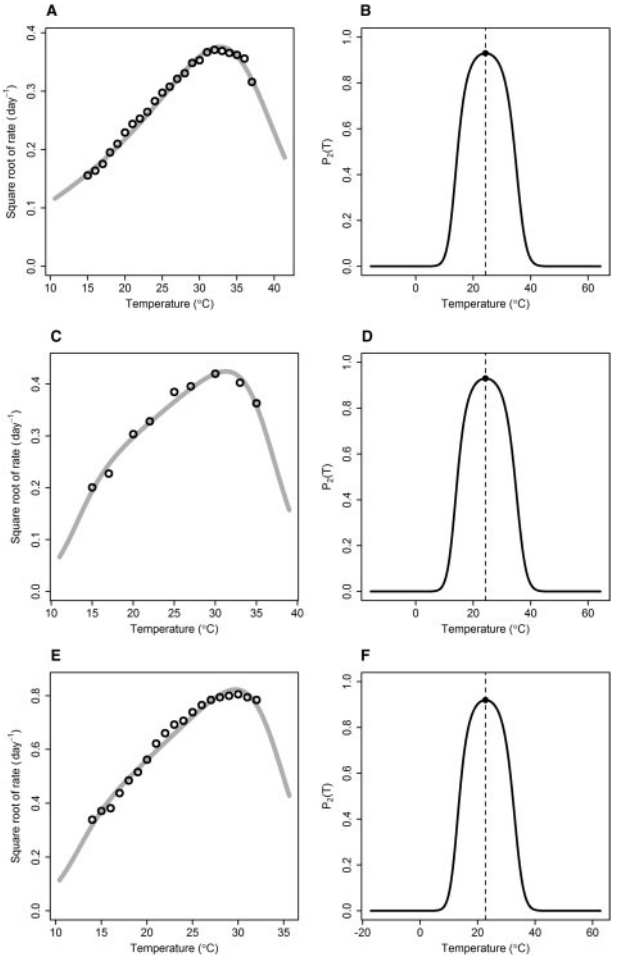

Fig. 3. Fitted square roots of developmental rates and the predicted probability of rate-controlling enzyme being in its native state using the revised ROR model (proposed by the present study). The species names in six panels are the same as those in Fig. 1. The small open circles represent the square roots of observed developmental rates; and the gray curve represents the predicted square roots of developmental rates.

different thermal performance of poikilotherms. Apparently, it is unsatisfactory to compare the model parameters obtained from using two different fitting methods for the same model. The fitting method of the revised ROR models used by the present study might over-fit the data because the square root curves (Fig. 3C and E) have an obvious protruding part that cannot be readily explained by thermodynamic theory. In the early ROR model (Ratkowsky et al. 2005), the curve will have little opportunity for making an unexplainable protruding part. For the early SSI model (Ikemoto 2008; Ikemoto et al. 2013), the fitted curves also have little opportunity

Table 4. Parameter estimate and goodness of fit using the revised five-parameter ROR model

Parameter	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5	Data set 6	Data set 7	Data set 8	Data set 9	Data set 10
T_{mes}	291.5	297.5	295.9	297.6	297.6	294.3	294.4	290.8	294.2	295.8
ΔH^*	5692.9	5833.0	4153.4	5957.7	5691.0	5606.1	4199.4	9837.8	4372.2	5239.9
n	246.7	545.6	606.1	510.5	613.4	457.7	348.6	453.5	802.1	672.4
$\Delta H_A^{\ddagger}$	85733.9	51817.5	69657.7	61896.6	68898.6	51594.2	48675.3	58706.4	57420.2	70345.4
T_H^*	378.7	380.6	356.3	382.3	378.5	377.3	356.6	443.2	359.2	372.1
ΔC_p	65.25	70.17	68.77	70.32	70.28	67.50	67.56	64.56	67.30	68.65
b	26.51	13.27	21.85	18.87	20.40	12.16	12.28	16.43	14.40	20.34
RSS	0.000975	0.000891	0.007345	0.004818	0.001367	0.000034	0.001292	0.000503	0.000032	0.000282
RMSE	0.006510	0.009950	0.019662	0.015924	0.009546	0.002213	0.010378	0.006760	0.001999	0.005593
χ^2	0.003717	0.002928	0.013074	0.006770	0.003320	0.000153	0.003925	0.001560	0.000158	0.001169
R^2	0.9915	0.9820	0.9850	0.9960	0.9906	0.9950	0.9881	0.9953	0.9975	0.9933

$T_S^* = 385.2$ K and $\Delta S^* = 18.1$ J·K^{-1}. T_H^* is one model parameter, not a constant. ΔC_p is calculated by equation (16). b is calculated by equation (20).

for producing a protruding part. Thus, we suggest using a fixed model system for multispecies comparisons of thermal performance. Meanwhile, the present study does not attempt to provide a better fitting method for the SSI model or the ROR model. It is possible to compare thermodynamic parameters among different data sets of temperature-dependent developmental rates of insects if the same model and fitting method are consistently applied to these data sets. For these two models that have different theoretical assumptions, it is somewhat unbelievable to compare the overlapped model parameters between them. The crucial step in our suggested fitting method is to build the parameter relationship between the numerator and the intrinsic optimum temperature using the quartic polynomial. In equation (8), when $T = T_\Phi$, the numerator approximately equals ρ_Φ. This parameter, ρ_Φ, is actually only affected by the quartic polynomial of T_Φ. Thus, the parameter of $\Delta H_A^{\ddagger}$ has no relationship with ρ_Φ and T_Φ. In equation (15), when $T = T_{mes}$, the numerator equals the quartic polynomial of T_{mes}, whereas T_{mes} has a relationship with ΔC_p according to equation (16). Meanwhile the parameters of b and $\Delta H_A^{\ddagger}$ will have a relationship with T_{mes} and ΔC_p. As a result, the relationships among these parameters reduce the fitting flexibility of the ROR model. The early fitting method proposed by Ratkowsky et al. (2005) can avoid such an issue, but the numerator of the ROR model can largely deviate from the observations around T_{mes} due to the large deviation of the denominator's reciprocal to 1 (e.g., Fig. 2F). Thus, the early version and the revised version both have advantages and disadvantages.

Either the SSI model or the ROR model has an intrinsic optimum temperature (namely, T_Φ and T_{mes}) that maximizes the probability of the enzyme being in its native state, but this temperature is lower than the temperature associated with the highest developmental rate. This phenomenon follows Jensen's inequality, and shows that the "suboptimal" value is actually optimal (Martin and Huey 2008). The temperature with the maximum developmental rate is not the intrinsic optimum temperature, which is in fact lower. The early version of the SSI model (Ikemoto et al. 2013) predicted a more than 6 °C difference between the intrinsic optimum temperature and the temperature of the highest developmental rate. The predicted differences between the intrinsic optimum temperatures and the temperatures of the highest developmental rate in the present study are also large. The early SSI fitting method suggests the tangent of the SSI model curve at the intrinsic optimum temperature is approximate to the straight line in the mid-temperature range (Ikemoto and Takai 2000). This exhibits a link of the thermodynamic curve to the straight line based on the law of effective heat accumulation. (T_Φ, ρ_Φ) can be regarded as a point in the SSI model curve, also approximately on a straight line at mid-temperature. For this reason, Ikemoto (2005, 2008) suggested using the linear equation to eliminate the parameter of ρ_Φ. In the present study, we use the quartic polynomial to replace the linear equation that can make ρ_Φ be closer approximate to the developmental rate at T_Φ. In addition, it can result in smaller RSS and achieve the global optimization to search the objective values of model parameters. In the present study, the SSI and ROR model both use the quartic polynomial and have the same model parameters, which can be used to compare the differences in the goodness of fit for different data sets. The SSI model appears to show its better goodness of fit and fitting flexibility on the condition that $P_2(T_\Phi) \approx 1$. However, the ROR model exhibits a better symmetry of the probability of the enzyme being in its native state at the expense of the goodness of fit. It seems that the symmetry only meets the psychological demands for aesthetics for geometry, but lacks the evidence that the symmetry represents the science. Thus, whether the probability of rate-controlling enzyme being in its native state is symmetrical requires further study.

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