Conditions for maxima and minima as inversion points in the temperature dependence of selection processes†

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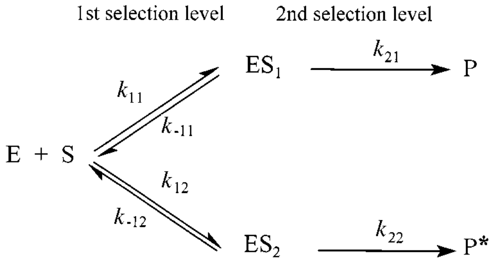
The analytical expression for deviations from linear behavior of logarithmic product ratios as a function of the reciprocal temperature (modified Eyring-plots) depends on the reason for the displacement. Therefore no generally valid formula exists that describes the experimentally observed inversion temperatures. In the case of the disturbance of the establishment of preequilibria, general conditions for the existence of inversion temperatures associated with maxima and minima are deduced. In addition it is shown that the inversion temperature is independent of the activation entropy values for the reaction of the starting materials to the intermediates ($\Delta S_{11}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$), but is dependent on the corresponding activation enthalpy values.

The examples discussed show that the limiting conditions intersecting points of the absolute rates are *not* suitable for a general description of the complex behavior of the nonlinear temperature dependency.

Selection processes play an important role in chemical reactions. Different kinds of product selectivity like chemo-, regio- or stereoselectivity can be found. For the formation of the products in a selection process at least two distinct reaction pathways are required. A simplified reaction sequence is shown in Scheme 1.



Scheme 1 General description of a selection process (E = catalytically active species; S = substrate; ES_i = intermediate; P, P* = reaction products; k_{ij} = rate constants).

In the first "selection level"‡ the intermediates ES_1 and ES_2 are formed reversibly, in the following irreversible step these intermediates react as second "selection level" to the products P and P*, respectively. This kinetic model can be applied to many different reactions, independent of whether the selection process is stoichiometric or catalytic. A well known catalytic example is the asymmetric hydrogenation of prochiral olefins with cationic ring chelates of Rh(I).[1] A more detailed review of selection models is given elsewhere.[2]

The aim of the preparative chemist is to obtain a strong differentiation between the possible reaction paths and thus a high selectivity. Reaction temperature is a readily available parameter for the control of selectivity. It is well known that the logarithmic product ratio is often not a linear function of the reciprocal temperature (modified Eyring-plot).§

Pracejus was the first to describe the nonlinear behavior of selectivity in a number of chemical reactions: *e.g.* the addition of achiral alcohols to unsymmetrical ketene derivatives catalyzed by chiral amines to give enantiomeric esters, and the nucleophilic addition of chiral primary amines to ketenes which leads to a pair of diastereomeric amides.[3–5]

Extreme values in the form of maxima and minima have been observed quite frequently for different selection processes. The temperature associated with an extreme value is called the *inversion temperature* ($T_{\mathrm{inv.}}$). Table 1 contains a selection of mostly recent examples that display an extreme value in the plot of the logarithmic product ratio as a function of reciprocal temperature. The knowledge and understanding of these "behavior patterns" is important both for the chemist in the laboratory and for the evaluation of different possible reaction sequences.[15],¶ In general, the selectivity of a reaction is at its highest at the inversion temperature associated with a maximum.

The experimental phenomenon of nonlinear behavior in the logarithmic product ratios as a function of the reciprocal temperature is described as the *isoinversion principle* empirically found by Scharf *et al.*[20,21] These authors rationalize nonlinear

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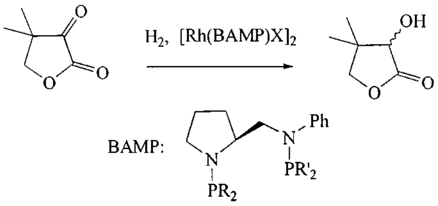
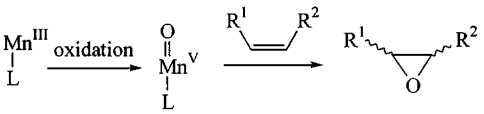
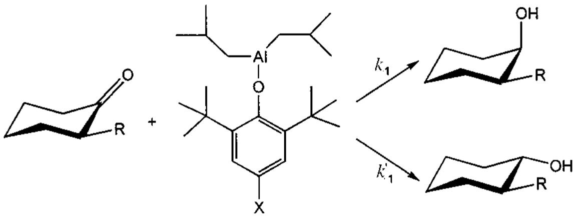
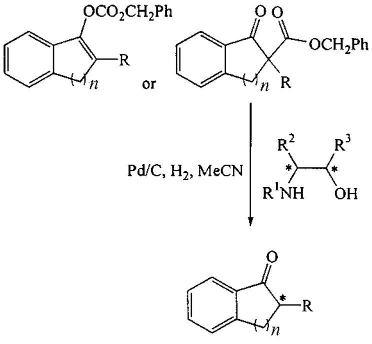
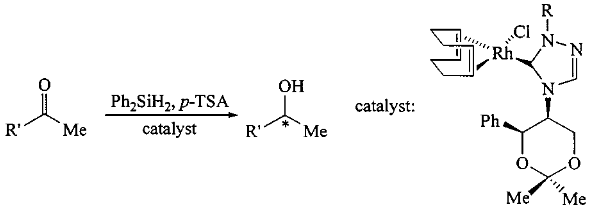
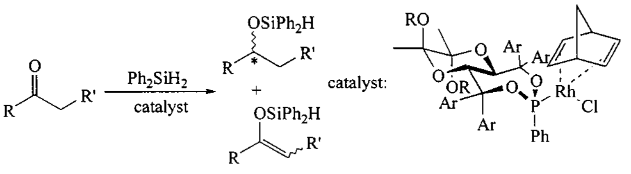
† Supplementary material (SUPPL. NO. 57475, 4 pp.) available from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). For direct electronic access see http://www.rsc.org/suppdata/p2/1999/175/.

‡ Originally[20,21] the first selection level was only characterized by the reaction of the starting materials to give the intermediates; however, we interpret it here as the result of all processes that characterize the *concentration ratio of the intermediates*. The division is arbitrary in both cases. The latter opinion, also adopted by Ridd *et al.*,[22,23] has the advantage of being oriented on the definition of the kinetic phenomenon selection as the ratio of the product formation rate by one reaction channel to the sum of rates of formation by both reaction pathways (rate being the product of concentration (first selection level) and rate constant (second selection level)).

§ Nonlinearities caused by systematic errors in the measurement, temperature dependent change of the mechanism or the well known temperature dependence of the activation parameters are excluded in this paper.

¶ The discussion about the mechanism of the important asymmetric dihydroxylation seems to be concluded.[16–19] Nevertheless, the corresponding nonlinear temperature dependence of the logarithmic product ratio as a function of the reciprocal temperature has not been explained to date.

Table 1 Selection processes with extrema in the temperature dependence of logarithmic product ratios

Process	Reaction scheme	Ref.
Catalytic, asymmetric ketone hydrogenation (Rh-complex as catalyst)		6
Asymmetric olefin epoxidation (Mn–salen-catalyst)		7[a]
Diastereoselective reduction of cyclohexanones (diisobutylaluminium phenoxides)		11
Asymmetric protonation of enolic species		12
Asymmetric hydrosilylation of methyl ketones (Rh-complexes)		13
Asymmetric hydrosilylation of ketones (Rh-complexes)		14

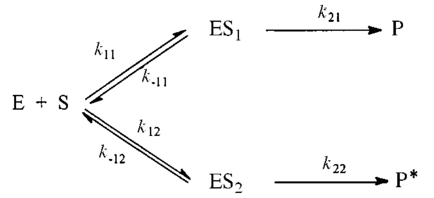
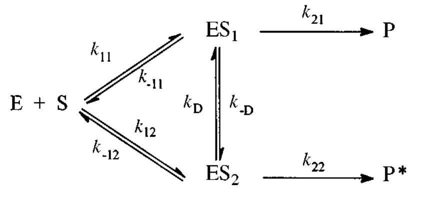
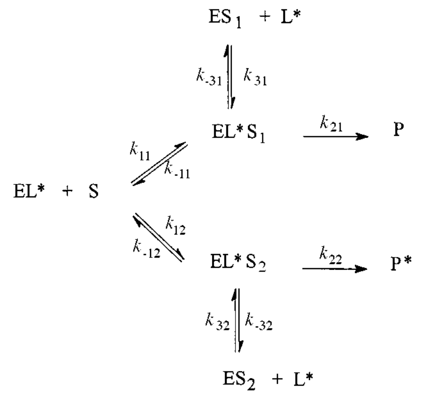
[a] For similar epoxidations linear Eyring-plots are observable. For a more detailed discussion see refs. 8–10.

temperature behavior by postulating that a change in the dominance of activation enthalpy differences ($\Delta\Delta H^{\ddagger}$) and activation entropy differences ($\Delta\Delta S^{\ddagger}$) occurs at different levels of selection in different temperature domains. According to Ridd *et al.*[22,23] a sudden change in the dominance of selection levels is unlikely. Their interpretation of experimental results, which show a nonlinear behavior of the logarithmic product ratios as a function of the reciprocal temperature for the selection model shown in Scheme 1, is based simply on changes in the rate-determining steps.

Recently, Gypser *et al.*[24] discussed the isoinversion principle in terms of the temperature dependence of the *absolute rates* for each reaction channel. A practical problem is the knowledge of the temperature dependence for a single reaction channel. Previously we described a concept which allows the determination of the temperature dependence of individual reaction pathways based on separating the nonlinear temperature dependence of the logarithmic product ratios of selection processes from the overall-activity *and* selectivity measurements.[25]

The interpretation of the experimentally well-established phenomenon of nonlinear temperature behavior, in our opinion, necessitates one distinguishing whether the relevant irreversible product formation in the selection process is the result of: 1. more than one reaction pathway, or 2. only a single reaction pathway.[26] Examples of the first case are characterized by the occurrence of more than two intermediates. A typical example is the asymmetric hydrogenation of prochiral olefins with Rh(I)-complexes using C_1-symmetrical chiral ligands: the formation of *two pairs of diastereomeric substrate complexes* has to be taken into account.[27] It is also possible that more than one substrate exists, for example as the result of an iso-

Table 2 Ratios of intermediates for different selection models which can lead to a nonlinear dependence of logarithmic product ratios as a function of reciprocal temperature

Model	Ratio of intermediates
	$\frac{[ES_1]}{[ES_2]} = \frac{k_{11}(k_{-12} + k_{22})}{(k_{-11} + k_{21})k_{12}}$ (disturbance of the establishment of preequilibria)
	$\frac{[ES_1]}{[ES_2]} = \frac{k_{11}(k_{-12} + k_D) + k_D k_{12}}{k_{12}(k_{-11} + k_{-D}) + k_{-D}k_{11}}$ (intramolecular exchange processes, established equilibria)
	$\frac{[EL^*S_1]}{[EL^*S_2]} = \frac{(k_{31}[ES_1][L^*] + k_{11}[EL^*][S])(k_{-12} + k_{-32})}{(k_{-11} + k_{-31})(k_{32}[ES_2][L^*] + k_{12}[EL^*][S])}$ (ligand dissociation processes at intermediates, disturbed equilibria) (L* = selection inducing ligand)

merization, which leads to the same reaction product. Also the so called "Nonlinear Effects" in asymmetric synthesis, for an excellent very recently published review see ref. 28, are typical examples for the first case.

For the second case the nonlinear behavior of the logarithmic product ratios as a function of the reciprocal temperature can be *reduced* always to a nonlinear behavior of the logarithmic *intermediate ratio*, as discussed previously.[29] Moreover, it is also possible that both types of product formation take place simultaneously. Three reasons are given as possible causes for the nonlinear behavior of the intermediates as a function of reciprocal temperature: a) disturbance in the establishment of preequilibria, b) direct intramolecular exchange processes between the intermediates (reported both for asymmetric hydrogenations with five-membered[30] and seven-membered ring rhodium chelate complexes[27,31] and for asymmetric hydrocyanations[32]) and c) equilibria that involve selection inducing ligands. A detailed derivation of these causes has been published.[26]

The aim of the present work is to quantify the general conditions for the existence of inversion temperatures associated with *maxima and minima* or more generally for deviations from linear behavior in logarithmic intermediate ratios as a function of the reciprocal temperature.

The inversion temperatures are the temperatures at which a maximum or a minimum occurs in the modified Eyring-plot.[20,21] Mathematically, such a point is characterized by the fact that the first derivative of the functional dependence of the logarithmic product ratio with respect to the reciprocal temperature is equal to zero. If the selection involves two reaction channels as shown in Scheme 1 and the second selection level is rate-determining, the logarithmic product ratio can be calculated according to eqn. (1).

$$\ln\left(\frac{[P]}{[P^*]}\right) = \ln\left(\frac{[ES_1]}{[ES_2]}\right) + \ln\left(\frac{k_{21}}{k_{22}}\right) = \ln\left(\frac{[ES_1]}{[ES_2]}\right) + \left(\frac{\Delta H_{22}^{\ddagger} - \Delta H_{21}^{\ddagger}}{RT} + \frac{\Delta S_{21}^{\ddagger} - \Delta S_{22}^{\ddagger}}{R}\right) \quad (1)$$

The differentiation with respect to the reciprocal temperature results in the general form shown in eqn. (2a) and for an extreme value in eqn. (2b). While

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = \frac{d\left(\ln\frac{[ES_1]}{[ES_2]}\right)}{d\left(\frac{1}{T}\right)} + \frac{\Delta H_{22}^{\ddagger} - \Delta H_{21}^{\ddagger}}{R} = \frac{d\left(\ln\frac{[ES_1]}{[ES_2]}\right)}{d\left(\frac{1}{T}\right)} + \frac{\Delta\Delta H_{2i}^{\ddagger}}{R} \quad (2a)$$

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = 0 \quad (2b)$$

the slope of the straight line for the second selection level can be described as the difference in the activation enthalpies divided by R ($\Delta\Delta H_{2i}^{\ddagger}/R$) for this selection level, derivation of the logarithmic intermediate ratio with respect to the reciprocal temperature is more complicated. The real problem lies in the fact that there are different derivatives for the different reasons that lead to nonlinear behavior of the intermediates. The ratio of the intermediates will always be described by another functional relationship. Table 2 shows the intermediate ratios for different possibilities that lead to a nonlinear ratio of intermediates.

We will now consider only extreme values, which are based on a shift of the rate-determining step, which corresponds to a disturbance in the establishment of intermolecular pre-equilibria (entry 1 in Table 2). In this case the precise condition for an extreme value of the logarithmic product ratios in the Eyring-plot is described by eqn. (3) (see Supplementary Material).†

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = \Delta H_{12}^\ddagger + A(\Delta H_{22}^\ddagger - \Delta H_{-12}^\ddagger) - \Delta H_{11}^\ddagger - C(\Delta H_{21}^\ddagger - \Delta H_{-11}^\ddagger)$$

$$= 0 \quad \text{for a maximum or a minimum} \qquad (3)$$

$$\left(A = \frac{e^{\frac{-\Delta G_{-12}^\ddagger}{RT}}}{e^{\frac{-\Delta G_{-12}^\ddagger}{RT}} + e^{\frac{-\Delta G_{22}^\ddagger}{RT}}} = \frac{k_{-12}}{k_{-12} + k_{22}}, \qquad C = \frac{e^{\frac{-\Delta G_{-11}^\ddagger}{RT}}}{e^{\frac{-\Delta G_{-11}^\ddagger}{RT}} + e^{\frac{-\Delta G_{21}^\ddagger}{RT}}} = \frac{k_{-11}}{k_{-11} + k_{21}}\right)$$

When eqn. (3) is satisfied for a certain temperature, namely the inversion temperature ($T_{\text{inv.}}$), a maximum or a minimum results in the logarithmic product ratio as a function of reciprocal temperature. To distinguish between a maximum and a minimum the value of the second derivative with respect to $1/T$ is determined once more. The distinction becomes clearer when the region around the inversion temperature is examined. For a maximum the value for the derivative of the logarithmic product ratio with respect to the reciprocal temperature must be larger or smaller than zero in the high-temperature region (to the left of the inversion temperature) or the low-temperature region (to the right of the inversion temperature), respectively, eqn. (4).

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = \left(-\frac{d\left(\ln\frac{[P^*]}{[P]}\right)}{d\left(\frac{1}{T}\right)}\right)$$

$$\begin{array}{ll} \begin{array}{l} >0 \text{ in the high temperature region} \\ <0 \text{ in the low temperature region} \end{array} & \text{maximum} \\ & \\ \begin{array}{l} <0 \text{ in the high temperature region} \\ >0 \text{ in the low temperature region} \end{array} & \text{minimum} \end{array} \qquad (4)$$

Eqn. (4) also clarifies the relation between maxima and minima. A maximum in the plot of ln([P]/[P*]) against $1/T$ corresponds to a minimum in the plot ln([P*]/[P]) against $1/T$. The difference lies only in the sign of the corresponding activation parameters in eqn. (3).

The validity of eqn. (3) can easily be tested. In the case of established preequilibria ($k_{2i} \ll k_{-1i}$) the terms for A and C are almost equal to one. The resulting form of eqn. (3) in this case corresponds to the derivative of the logarithmic product ratio, if the preequilibria are not displaced in its establishment, eqn. (5). In this case the slope of the reciprocal temperature dependence is constant and therefore the reciprocal temperature dependence itself is linear. If $k_{2i} \gg k_{-1i}$ (*i.e.* the formation

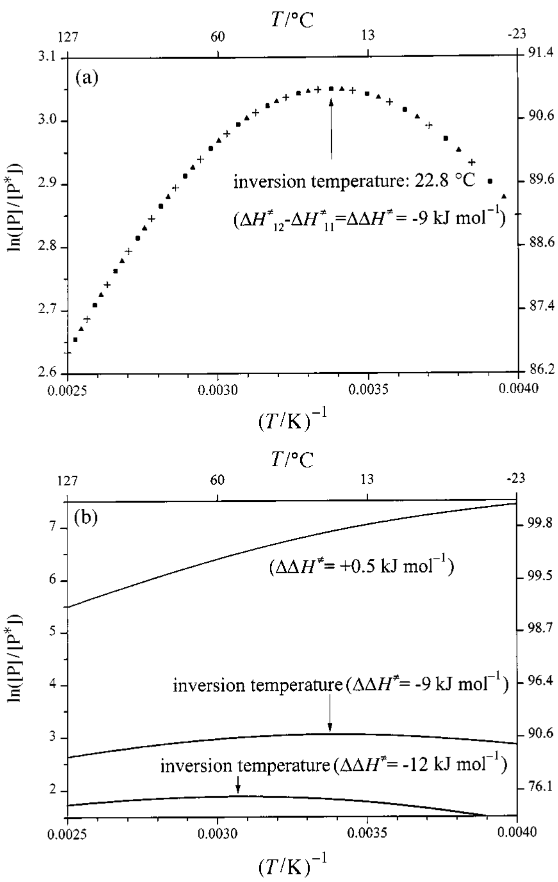


Fig. 1 a: Dependence of the logarithmic product ratios as functions of the reciprocal temperature according to eqn. (1) (intermediate ratio: Table 2, entry 1). Data from Table 3, columns a–c. b: Dependence of the logarithmic product ratios as functions of the reciprocal temperature according to eqn. (1) (intermediate ratio: Table 2, entry 1). Data from Table 3, column a (middle), d (bottom), e (top).

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = \Delta H_{12}^\ddagger + \Delta H_{22}^\ddagger - \Delta H_{-12}^\ddagger - \Delta H_{11}^\ddagger - \Delta H_{21}^\ddagger + \Delta H_{-11} = \text{const. (if } k_{2i} \ll k_{-1i}) \qquad (5)$$

of the products is only a function of the rate of the formation of the intermediates from the starting materials or in other words, the first selection level is rate-determining, for a more detailed discussion see Landis and Halpern[1] or Boudart *et al.*[33]), the result is that in the sense of a limiting consideration, A and C will be zero. Also in this case the temperature dependence is linear, eqn. (6). Eqns. (5) and (6) represent the slopes of the temperature dependence for the so called "limiting conditions".

$$\frac{d\left(\ln\frac{[P]}{[P^*]}\right)}{d\left(\frac{1}{T}\right)} = \Delta H_{12}^\ddagger - \Delta H_{11}^\ddagger = \text{const.} \quad (\text{if } k_{2i} \gg k_{-1i}) \qquad (6)$$

Eqn. (3) contains, within the terms A and C, the temperature at the extreme value of the logarithmic product ratio. By transforming and solving the equation, for example iteratively, the inversion temperature can be calculated when the $\Delta H_{ij}^\ddagger$ and $\Delta S_{ij}^\ddagger$ values are known. The analysis of eqn. (3) shows

Table 3 $\Delta H^‡$ (kJ mol^{-1}) and $\Delta S^‡$ (J mol^{-1} K^{-1}) values for the calculation of rate constants according to Scheme 1

	a	b	c	d	e	f	g	h	i	j	k	l	m
$\Delta H^‡_{11}$	*29*	*19*	*44*	*29*	*19.5*	29	29	29	29	29	29	30	48
$\Delta H^‡_{12}$	*20*	*10*	*35*	*17*	*20*	20	20	20	20	20	20	16.34	47
$\Delta S^‡_{11}$	*−71*	−71	−71	−71	−71	*−42*	*13*	*−71*	*−63*	*−79*	*−71*	−40	−100
$\Delta S^‡_{12}$	*−103*	−103	−103	−103	−103	*−74*	*−19*	*−111*	*−103*	*−103*	*−95*	−120	−100
$\Delta H^‡_{-11}$	54	54	54	54	54	54	54	54	54	54	54	50	38
$\Delta H^‡_{-12}$	56	56	56	56	56	56	56	56	56	56	56	30	38
$\Delta S^‡_{-11}$	−54	−54	−54	−54	−54	−54	−54	−54	−54	−54	−54	−30	60
$\Delta S^‡_{-12}$	−75	−75	−75	−75	−75	−75	−75	−75	−75	−75	−75	−60	60
$\Delta H^‡_{21}$	36	36	36	36	36	36	36	36	36	36	36	30	24
$\Delta H^‡_{22}$	57	57	57	57	57	57	57	57	57	57	57	25	27
$\Delta S^‡_{21}$	−113	−113	−113	−113	−113	−113	−113	−113	−113	−113	−113	−110	0
$\Delta S^‡_{22}$	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	−100	−80	0

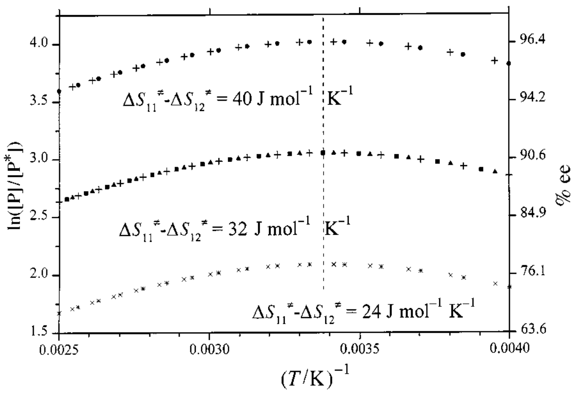


Fig. 2 Dependence of the logarithmic product ratios as functions of the reciprocal temperature according to eqn. (1) (intermediate ratio: Table 2, entry 1). Data from Table 3, column a, f, g (middle), h, i (top), j, k (bottom).

that the absolute values for the ΔH_{1i}'s are not important. The *difference* of these values ($\Delta H_{12}^‡ - \Delta H_{11}^‡ = \Delta\Delta H^‡$) is the essential feature. In Fig. 1a the results are plotted for different individual $\Delta H_{1i}^‡$ values but the differences $\Delta\Delta H^‡$ are the same (Table 3, columns a–c). As expected, the curves are indistinguishable. On the other hand, Fig. 1b represents the results for unequal differences in the $\Delta H_{1i}^‡$ values. A change in the differences between the corresponding values leads to an alternative temperature behavior. If the values for $\Delta H_{1i}^‡$ do not fulfill eqn. (3) no extreme value is observed (upper curve in Fig. 1b, Table 3, column e).

What is truly interesting about eqn. (3) is that the values for $\Delta S_{11}^‡$ and $\Delta S_{12}^‡$ are not included. All the other $\Delta S_{ij}^‡$ values are included in the terms A and C from eqn. (3). This means that $\Delta S_{11}^‡$ and $\Delta S_{12}^‡$ have no influence on the existence of maxima and minima and the corresponding inversion temperature. However, this does *not* mean that the values for $\Delta S_{11}^‡$ and $\Delta S_{12}^‡$ do not have any influence on the experimentally observed selectivity. To illustrate this graphically (Fig. 2) the temperature dependence of the resulting logarithmic product ratios were calculated from eqn. (1) (intermediate ratio: Table 2, entry 1) and the corresponding values are given in the columns a and f–k in Table 3. The results confirm the independence of the inversion temperature of $\Delta S_{11}^‡$ and $\Delta S_{12}^‡$. Furthermore it becomes clear that the degree of selection is only determined by the degree of difference in activation entropies of the reaction of the starting materials to give the intermediates ($\Delta S_{11}^‡ - \Delta S_{12}^‡$) and not by the corresponding absolute values. The larger the difference in activation entropy, the larger the experimentally obtainable selectivity will be, given that the other values are constant.

The results above can be summarized as follows. The difference of the values $\Delta H_{12}^‡ - \Delta H_{11}^‡$ influences the inversion temperature *and* the experimentally observable selectivity, while the corresponding value for the activation entropy influences only the selectivity but *not* the inversion temperature itself or in a more general sense the slope of the nonlinear temperature dependence.

It should be noted that the second derivative of the logarithmic product ratio with respect to the reciprocal temperature does not contain the complete activation for conversion of the starting materials to the intermediates; $\Delta H_{11}^‡$ and $\Delta H_{12}^‡$ as well as $\Delta S_{11}^‡$ and $\Delta S_{12}^‡$. This means that whether a maximum or a minimum is present does not depend on this stage of the selection process.

The considered maxima and minima are special cases. The general case is a nonlinearity of the logarithmic product ratios as a function of reciprocal temperature. In other words, because the values between zero and one for A and/or C in eqn. (3) are temperature dependent, the slope in the modified Eyring-plot is not constant. That is the factors A and C in eqn. (3) contain the "individuality" of the different reaction pathways. From this generally valid point, it follows that both reaction pathways can behave with a different temperature dependence. However, macroscopically what is observed is the sum of both reaction pathways, with at least one channel that is nonlinear.

The same considerations are, in principle, also valid if the temperature dependence of single product formation rates (absolute rates) is analyzed instead of product ratios (relative rates) as used here. Examples for nonlinear behavior of the temperature dependence of absolute rates are well known.[34–37] However, caution should be used in defining the inversion temperature.

Gypser *et al.* discussed the nonlinear behavior in the temperature dependence in terms of the absolute rates. According to these authors the "inversion temperature" for relative rates is determined in the following manner: "If the inversion temperatures of the absolute rates are identical for two corresponding reaction paths, the inversion temperature for the relative rates is equal to those for the absolute rates".[24] The inversion temperatures of the absolute rates are defined as the intersecting points of the limiting conditions for the considered reaction sequence, eqn. (7).[24] (A more detailed description of the limiting conditions can be found in ref. 23.)

$$T_{\text{int ers.p.abs.rates}} = \frac{\Delta H_{2i}^‡ - \Delta H_{-1i}^‡}{\Delta S_{2i}^‡ - \Delta S_{-1i}^‡} \quad (i = 1, 2) \qquad (7)$$

Fig. 3a presents the Eyring-plots of the absolute rates and the corresponding limiting conditions using the $\Delta H_{ij}^‡$ and $\Delta S_{ij}^‡$ values of column a in Table 3 for the calculation of the rate constants. Fig. 3a shows that the points of intersection of these limiting conditions lie for each reaction pathway at 250 K ($1/T = 0.004$ K^{-1}). Fig. 3b shows the temperature dependency of the relative rates. According to the statement cited above the inversion temperature of the relative rates should be 250 K. It

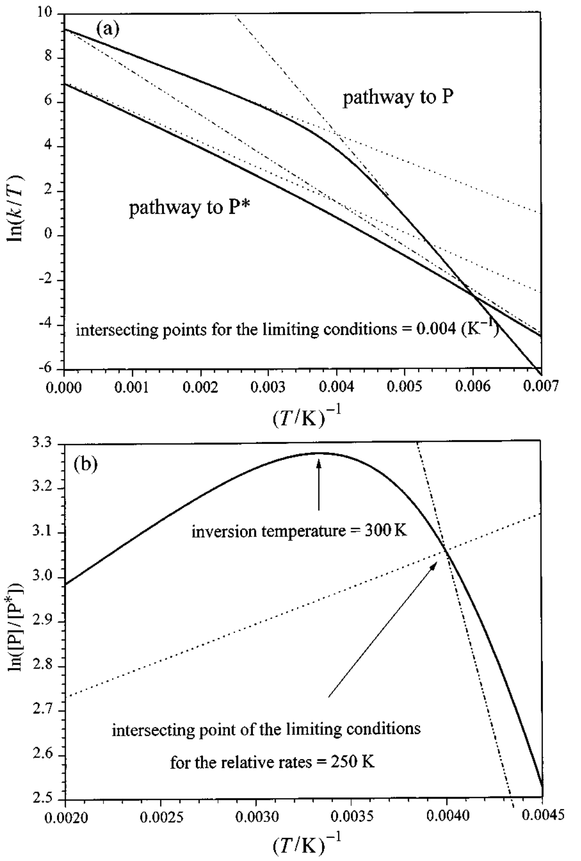


Fig. 3 a: Eyring-plots of the absolute rates and the corresponding limiting conditions (Table 3, column l). b: Eyring-plots of the relative rates and the corresponding limiting conditions (Table 3, column l).

is true that the limiting conditions of the relative rates intersect at 250 K, but the logarithmic product ratio as a function of the reciprocal temperature actually *inverts*—in the strict sense of the word—at 300 K ($1/T = 0.00333$ K^{-1}); 50 K above the value expected according to Gypser *et al.* In accordance with Fig. 3b, eqn. (3) leads also to this value.

Moreover it was said in ref. 24: "In the case of unequal inversion temperatures for the absolute rates, the inversion temperature for the relative rates has to be somewhere in between those for the absolute rates." On the basis of eqn. (7) it follows for the example *C* from ref. 23 (column m in Table 3) that the inversion temperature values of the absolute rates are 233.3 K (0.00429 K^{-1}) and 183.3 K (0.00545 K^{-1}) respectively. Hence, this is a typical example of the behavior described above. In Fig. 4 the logarithmic product ratio is graphically depicted as a function of the reciprocal temperature. The maximum of the relative rates does not lie between the inversion temperatures of the absolute rates, emphasized by the hatched area in Fig. 4. Rather, this maximum lies outside the expected area, at 290.7 K ($1/T = 0.00344$ K^{-1}). In this example the limiting conditions intersection point for the relative rates (T_{lcip}) lies in the origin of coordinates.[38] Furthermore, one easily can imagine conditions under which the limiting conditions of the relative rates do not intersect at all.

The discrepancy in the discussion above is caused by different definitions of the "inversion temperature". On the one hand it is described as an experimentally observable temperature connected with an extreme value, for example a maximum which represents maximum available selectivity, on the other hand it is discussed as an intersection of the limiting conditions *without practical relation*. The examples above show that the two definitions of inversion temperature lead to different results. So, the different points of view are not reducible to a simple semantic problem. This is exemplified further in the following example. Gypser *et al.*[24] pointed out that "The value of the inversion temperature is independent of the activation parameters of the first selection level (represented by the activation parameters $\Delta H_{1i}{}^{\ddagger}$ and $\Delta S_{1i}{}^{\ddagger}$)." This statement is not true; eqn. (3) does not contain the $\Delta S_{1i}{}^{\ddagger}$, but rather the $\Delta H_{1i}{}^{\ddagger}$, values, see the discussion above in connection with Fig. 1b.

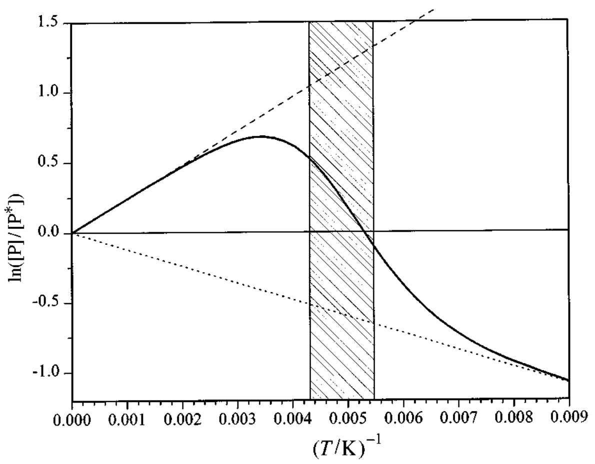


Fig. 4 Logarithmic product ratios as functions of the reciprocal temperature and the limiting conditions (Table 3, column m, original data according to ref. 23).

In summary, we have established that the analytical expression for an inversion temperature in relation to maxima and minima depends on the reason for the displacement. Therefore no generally valid formula, as reported, exists that describes the experimentally observed inversion temperatures. In the case of a disturbance in the establishment of preequilibria, we have shown that the inversion temperature is independent of the activation entropy values for the reaction of the starting materials to the intermediates ($\Delta S_{11}{}^{\ddagger}$ and $\Delta S_{12}{}^{\ddagger}$), but is dependent on the corresponding activation enthalpy values.

The examples discussed show that the limiting conditions intersecting points of the absolute rates, are *not* suitable for a general description of the complex behavior of the nonlinear dependency of logarithmic product ratios as a function of the reciprocal temperature.

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38 $$T_{\mathrm{lcip}} = \frac{\Delta H_{21}^{\ddagger} - \Delta H_{-11}^{\ddagger} - (\Delta H_{22}^{\ddagger} - \Delta H_{-12}^{\ddagger})}{\Delta S_{21}^{\ddagger} - \Delta S_{-11}^{\ddagger} - (\Delta S_{22}^{\ddagger} - \Delta S_{-12}^{\ddagger})} = \frac{(24000 - 38000) - (27000 - 38000)}{(0 - 60) - (0 - 60)}$$

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