A reassessment of the isoinversion relationship

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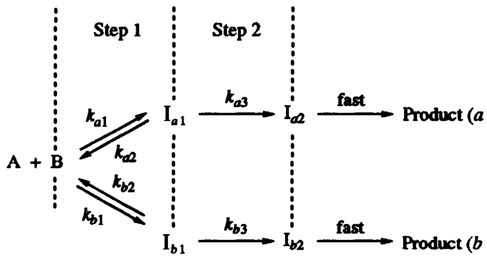
Calculations have been carried out on model systems with two potentially rate determining steps on a single reaction path. Taking the ratio of the diastereoisomers as P, the maxima found on plots of ln P *vs.* $1/T$ are shown to derive from the intersection of a line characteristic of one rate-determining step and a second line characteristic of the transitional region in which no single step is rate-determining. On this interpretation, the quantities previously calculated from the difference between the slopes of these lines and termed $\delta\Delta\Delta H^\ddagger$ and $\delta\Delta\Delta S^\ddagger$ have no simple physical meaning. The isoinversion relationship involving these quantities is not therefore a conventional enthalpy–entropy relationship. For those sets of reactions that involve little change in the inversion temperature, the isoinversion relationship is shown to be a necessary consequence of the geometry of the plot and the definition of the terms.

There is currently great interest in reactions in which a molecule A reacts with another molecule B to form a pair of diastereoisomers.[1] The symbol P is used to denote the ratio of the diastereoisomers and plots of ln P *vs.* $1/T$ are frequently found to be linear. This is as expected from the Eyring equation, for the slope of the plot is then equal to $-\Delta\Delta H^\ddagger/R$ where $\Delta\Delta H^\ddagger$ is the difference between the enthalpies of activation of the reactions leading to the two diastereoisomers. However, some plots of ln P *vs.* $1/T$ have maxima[1c,2] and this has been attributed to a change in the rate-determining step as the temperature is varied. Examples of such plots in thermal reactions include the osmium tetroxide asymmetric dihydroxylation of olefins[2] and the diastereoselective reduction of 2-*tert*-butylcyclohexanone.[1c] In photochemical reactions, particular attention has been paid to the Paternò–Büchi reaction of chiral phenylglyoxalates with cyclic olefins.[3] The difference between the slopes of the lines on either side of the maximum has been used to calculate $\delta\Delta\Delta H^\ddagger$ (the change in the value $\Delta\Delta H^\ddagger$ between the two rate determining steps) and the difference between the intercepts of these lines on the $T = \infty$ axis has been used to calculate $\delta\Delta\Delta S^\ddagger$ (the change in the corresponding entropy term $\Delta\Delta S^\ddagger$ between the two rate determining steps). In a series of related reactions, plots of $\delta\Delta\Delta H^\ddagger$ *vs.* $\delta\Delta\Delta S^\ddagger$ have been found to be linear and this relationship has been termed the isoinversion principle[3] or, more recently, the isoinversion relationship.[4] Studies of the isoinversion relationship up to 1991 have been comprehensively reviewed.[4]

However, the experimental results imply a curiously abrupt change in the rate-determining step as the temperature is varied and this has led us to put forward an alternative interpretation in which the slope of the line on one side of the maximum comes from the transitional region in which no single stage of the reaction can be considered as rate-determining.[5] In terms of the temperature range involved, this transitional region can be very broad for the difference in the activation energies of the reactions of a relatively high energy intermediate can be quite small. On this interpretation, the slopes of the plots of ln P *vs.* $1/T$ are not necessarily related to the value of $\Delta\Delta H^\ddagger$ for any single rate-determining step. The present paper is concerned with the consequences of this reinterpretation and, in particular, with the reason why plots of the quantities previously termed $\delta\Delta\Delta H^\ddagger$ and $\delta\Delta\Delta S^\ddagger$ should be linear.

The kinetic form

As before,[5] we have taken the reaction paths shown in Scheme 1 as a basis for our calculations. On this reaction path, the intermediates I exist as two diastereoisomers labelled a and b.



Scheme 1

In choosing this reaction scheme, we have had in mind one of the interpretations put forward for the osmium tetroxide asymmetric hydroxylation of alkenes[1a,2] but the arguments are, of course, more general.

On this reaction scheme, the paths leading to the two diastereoisomers are independent and so, assuming the concentrations of the intermediates I_{a1} and I_{b1} to be small, the kinetic form is given by eqn. (1). Since the reactions leading to

$$-\frac{\mathrm{d}c_A}{\mathrm{d}t} = \left(\frac{k_{a1}k_{a3}}{(k_{a2} + k_{a3})} + \frac{k_{b1}k_{b3}}{(k_{b2} + k_{b3})}\right)c_A c_B = (k_{a(\mathrm{obs})} + k_{b(\mathrm{obs})})\, c_A c_B \qquad (1)$$

the two diastereoisomers have the same kinetic form, the ratio of the two diastereoisomers should be constant during reaction and is given by eqn. (2). The symbol a will normally be assigned

$$P = \frac{k_{a(\mathrm{obs})}}{k_{b(\mathrm{obs})}} = \frac{k_{a1}k_{a3}(k_{b2} + k_{b3})}{(k_{a2} + k_{a3})k_{b1}k_{b3}} \qquad (2)$$

to the diastereoisomer that is predominant at the higher temperatures.

Eqn. (2) has two limiting forms, depending on the relative magnitudes of k_2 and k_3; these are shown in eqns. (3) and (4).† The conditions for eqn. (3) make Step 1 rate determining, and those for eqn. (4) make Step 2 rate determining.

$$\text{limit}\ k_2/k_3 \longrightarrow 0 \qquad P = \frac{k_{a1}}{k_{b1}} \qquad (3)$$

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† The symbols a and b are omitted from rate coefficients and intermediates when reference is made to both diastereoisomers.

$$\text{limit } k_3/k_2 \longrightarrow 0 \qquad P = \frac{k_{a1}k_{a3}k_{b2}}{k_{b1}k_{b3}k_{a2}} \tag{4}$$

The activation parameters

The consequences of these equations on the activation parameters can be seen by expressing each rate coefficient in terms of the Eyring equation.[6] This is shown for the rate coefficient k_{a1} in eqn. (5) where the symbols have their usual significance.[6]

$$k_{a1} = \left(\frac{k_B T}{h}\right) e^{\frac{\Delta S^{\ddagger}_{a1}}{R}} e^{\frac{-\Delta H^{\ddagger}_{a1}}{RT}} \tag{5}$$

It is convenient to define the quantities $\Delta\Delta H^{\ddagger}_1$, $\Delta\Delta S^{\ddagger}_1$, $\Delta\Delta H^{\ddagger}_2$ and $\Delta\Delta S^{\ddagger}_2$. by eqns. (6)–(9). The values of ln P under the limiting conditions are then given by eqns. (10) and (11).

$$\Delta\Delta H^{\ddagger}_1 = \Delta H^{\ddagger}_{a1} - \Delta H^{\ddagger}_{b1} \tag{6}$$

$$\Delta\Delta S^{\ddagger}_1 = \Delta S^{\ddagger}_{a1} - \Delta S^{\ddagger}_{b1} \tag{7}$$

$$\Delta\Delta H^{\ddagger}_2 = \Delta H^{\ddagger}_{a1} + \Delta H^{\ddagger}_{a3} + \Delta H^{\ddagger}_{b2} - \Delta H^{\ddagger}_{a2} - \Delta H^{\ddagger}_{b1} - \Delta H^{\ddagger}_{b3} \tag{8}$$

$$\Delta\Delta S^{\ddagger}_2 = \Delta S^{\ddagger}_{a1} + \Delta S^{\ddagger}_{a3} + \Delta S^{\ddagger}_{b2} - \Delta S^{\ddagger}_{a2} - \Delta S^{\ddagger}_{b1} - \Delta S^{\ddagger}_{b3} \tag{9}$$

$$\text{limit } k_2/k_3 \longrightarrow 0 \qquad \ln P = \frac{-\Delta\Delta H^{\ddagger}_1}{RT} + \frac{\Delta\Delta S^{\ddagger}_1}{R} \tag{10}$$

$$\text{limit } k_3/k_2 \longrightarrow 0 \qquad \ln P = \frac{-\Delta\Delta H^{\ddagger}_2}{RT} + \frac{\Delta\Delta S^{\ddagger}_2}{R} \tag{11}$$

One or both of the limiting eqns. (10) and (11) have been given many times in the literature[3,4,7,8] but the derivation above has been set out because the quantities $\Delta\Delta H^{\ddagger}_1$, $\Delta\Delta S^{\ddagger}_1$, $\Delta\Delta H^{\ddagger}_2$ and $\Delta\Delta S^{\ddagger}_2$ have usually been said to correspond to the enthalpy and entropy in each of the partial selectivity steps.[4] There is a useful distinction to be made here: the definitions in eqns. (8) and (9) show that $\Delta\Delta H^{\ddagger}_2$ and $\Delta\Delta S^{\ddagger}_2$ are not the enthalpic and entropic discrimination in the second step of the reaction but the overall enthalpic and entropic discrimination when the second step is rate determining.

The quantities $\delta\Delta\Delta H^{\ddagger}$ and $\delta\Delta\Delta S^{\ddagger}$ are defined[4] by eqns. (12) and (13)‡ but have been determined experimentally from the

$$\delta\Delta\Delta H^{\ddagger} = \Delta\Delta H^{\ddagger}_1 - \Delta\Delta H^{\ddagger}_2 \tag{12}$$

$$\delta\Delta\Delta S^{\ddagger} = \Delta\Delta S^{\ddagger}_1 - \Delta\Delta S^{\ddagger}_2 \tag{13}$$

slopes and intercepts of the lines on either side of a maximum in a plot of ln P *vs.* $1/T$. It is now necessary to consider whether these lines do, in fact, correspond to the limiting eqns. (10) and (11).

Calculations on model systems

A change with temperature in the rate-determining step in the reactions of Scheme 1 requires a change in the ratio k_2/k_3 from $k_2 \ll k_3$ to $k_2 \gg k_3$. This can obviously be achieved by assigning different enthalpies of activation to the two reactions but the fact that the ratio k_2/k_3 must pass through unity imposes a restriction on the maximum value of $(\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_3)$ that can be used. In Scheme 1, reaction 2 is a dissociation and reaction 3 is a rearrangement; this distinction has been recognised in the majority of the following calculations by assigning a value of *ca.* 60 J deg^{-1} mol^{-1} to reaction 2 and a value of *ca.* 0 J deg^{-1} mol^{-1} to reaction 3. The large negative entropy of activation for the first step accords with that found in the Diels–Alder reaction[9] and the other parameters have been adjusted to give a change in the rate determining step over the temperature range listed and a half life of *ca.* 2 min to 1 h with reactant concentrations of 0.1 mol dm^{-3} at 20 °C. For simplicity, the back reaction (rate coefficient k_2) has been assumed to lead to no discrimination between the diastereoisomers (except for the last reaction in Table 1). This absence of this assumption would not change the conclusions outlined below.

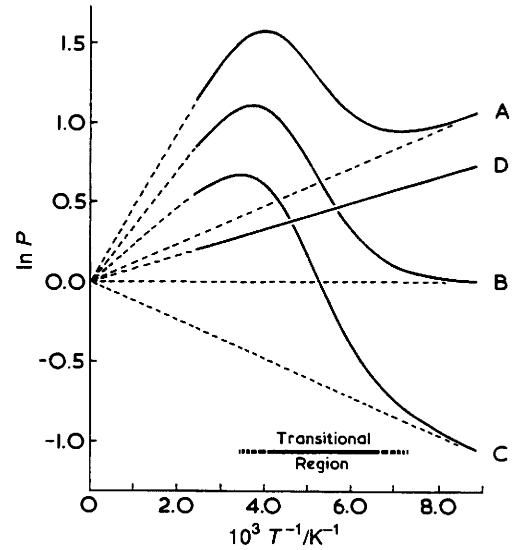

Fig. 1 Examples of ln P *vs.* $1/T$ plots resulting from enthalpic discrimination between the diastereoisomers. The parameters are listed in Table 1. The broken lines are the limiting lines for each plot defined by eqns. (10) and (11).

Consider first reactions with only enthalpic discrimination between the diastereoisomers. The plots in Fig. 1 show the variation of ln P with $1/T$ and the corresponding limiting lines derived from eqns. (10) and (11) for four reactions corresponding to the parameters listed in Table 1. The rate determining step changes from Step 1 to Step 2 (Scheme 1) as the temperature is increased.

Although the plots match the limiting equations at the extremes of the temperature range (− 160 to 150 °C), for plots A–C there is also a broad transitional region. The width of this region depends on $(\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_3)$. The plots also show that the slope in the transitional region is not simply related to the limiting slopes: indeed, the transitional slope remains negative when the slope corresponding to eqn. (10) changes from positive (plot A) through zero (plot B) to negative (plot C). The slope in the transitional region is determined in part by the relative isomer discrimination (enthalpic plus entropic) at the two rate determining steps and partly by the value of $(\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_3)$.

Plot B illustrates what happens when there is no discrimination between the isomers in step 1. A quite different type of plot occurs when the discrimination is limited to the forward reaction in step 1 (plot D): the two limiting lines are superimposed and the points from eqn. (2) lie on this line.

When the isomer discrimination is purely entropic, the limiting slopes are horizontal but there can still be a broad transitional region as illustrated in Fig. 2. The parameters for

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‡ This definition is the same as that given in ref. 4 but the subscripts are interchanged since in that reference the subscript 1 is used to refer to the rate determining step at the higher temperatures.

Table 1 Parameters $\Delta S^\ddagger$ (J deg^{-1} mol^{-1}) and $\Delta H^\ddagger$ (kJ mol^{-1}) used for the plots in Figs. 1–4

	Plot									
Parameter	A	B	C	D	E	F	G	H	I	J
$\Delta S^\ddagger_{a1}$	−100	−100	−100	−100	−100	−87	−100	−100	−85	−75
$\Delta S^\ddagger_{b1}$	−100	−100	−100	−100	−115	−100	−100	−100	−100	−107
$\Delta H^\ddagger_{a1}$	47	48	48	47.3	48	48	48	48	48	47.5
$\Delta H^\ddagger_{b1}$	48	48	47	48	48	48	48	48	47	45
$\Delta S^\ddagger_{a2}$	60	60	60	60	80	80	80	45	60	85
$\Delta S^\ddagger_{b2}$	60	60	60	60	80	80	80	45	60	55
$\Delta H^\ddagger_{a2}$	38	38	38	38	35	35	35	35	38	38
$\Delta H^\ddagger_{b2}$	38	38	38	38	35	35	35	35	38	38
$\Delta S^\ddagger_{a3}$	0	0	0	0	0	0	10	10	−8	0
$\Delta S^\ddagger_{b3}$	0	0	0	0	25	0	0	0	0	0
$\Delta H^\ddagger_{a3}$	24	24	24	27	24	24	24	24	25.5	25.5
$\Delta H^\ddagger_{b3}$	27	27	27	27	24	24	24	24	27	28

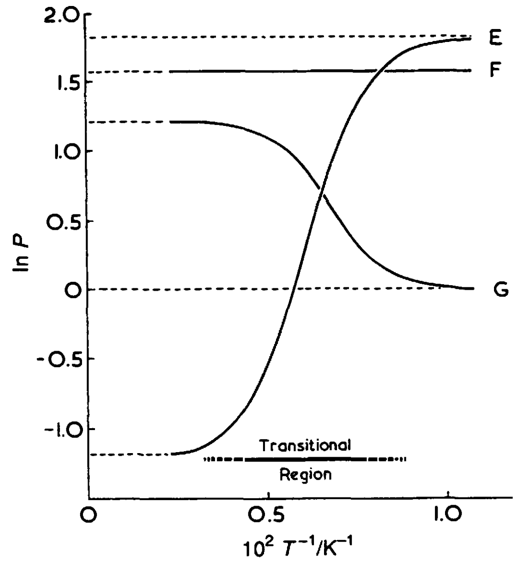

Fig. 2 Examples of ln P *vs.* $1/T$ plots resulting from entropic discrimination between the diastereoisomers. For other details see Fig. 1.

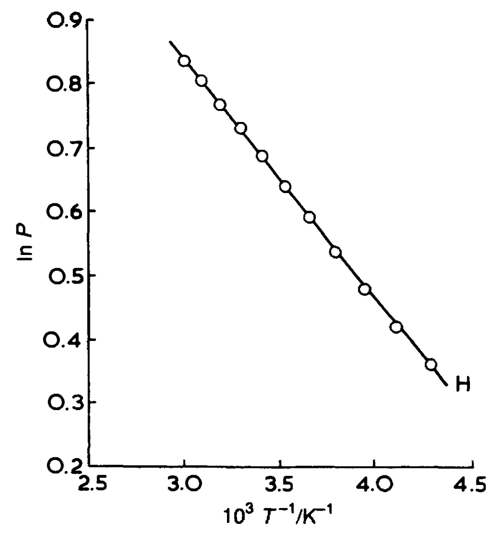

Fig. 3 An example of the good approximation to a linear plot of ln P *vs.* $1/T$ obtained in the transitional region as a result of entropic discrimination. The line is straight and the points are calculated from the parameters for reaction H in Table 1 for the temperature range −40 to 60 °C.

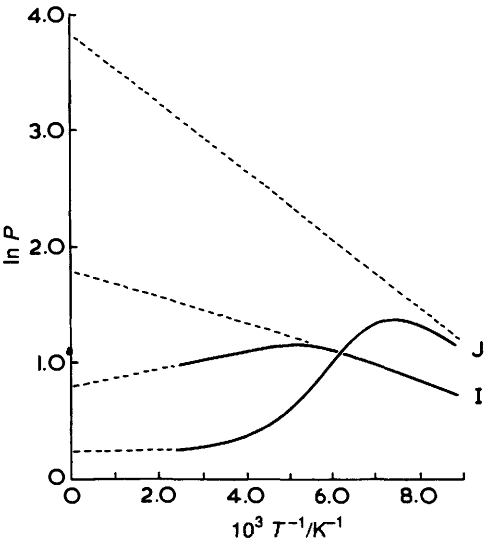

Fig. 4 Examples of ln P *vs.* $1/T$ plots resulting from both enthalpic and entropic discrimination between the diastereoisomers. For other details see Fig. 1.

these plots are included in Table 1. Plot G also illustrates that the form of these curves is retained when only step 2 gives discrimination between the isomers. When the discrimination is limited to the forward reaction of step 1, the two limiting lines become identical and all of the points from eqn. (2) lie on that line (plot F).

The linearity that is possible in the transitional region is illustrated by the straight line (correlation coeff. 0.9999) generated by points calculated for reaction H over the temperature range −40 to 60 °C (Fig. 3). This plot stems from entropic discrimination in the second transition state.

When both enthalpic and entropic discrimination is present, the plots of ln P *vs.* $1/T$ can take several other forms. Two are illustrated in Fig. 4. In plot I, a maximum is present but the slope in the transitional region is close to that of the second limiting line and so here the slopes on either side of the maximum do accord reasonably well with those calculated from eqns. (10) and (11). This accord between the transitional and limiting slopes does, however, require a very careful choice of the relevant parameters and should seldom be observed. Plot J, in Fig. 4, shows a maximum in which the positive slope comes from the transitional region and the negative slope corresponds to one of the limiting lines. Examples of plots showing minima have not been given since whether a maximum or a minimum is observed depends on the selection of the diastereoisomer assigned as a in the definition of P by eqn. (2).

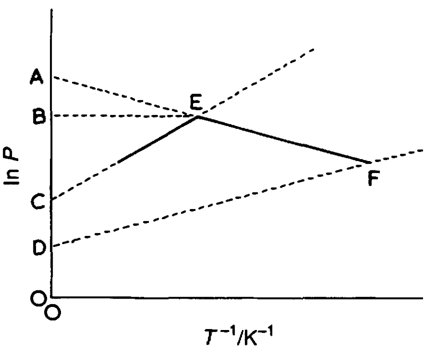

Fig. 5 A diagrammatic representation of a plot of ln *P vs.* $1/T$ of the type shown in Fig. 1, reaction A. For details see text.

The isoinversion relationship

The literature values[4] of $\delta\Delta\Delta H^{\ddagger}$ and $\delta\Delta\Delta S^{\ddagger}$ have been calculated from the slopes of the lines on either side of a maximum in plots of ln *P vs.* $1/T$. This involves the assumption that these lines correspond to the limiting lines defined by eqns. (10) and (11). Since this assumption can only be true under exceptional circumstances (see above), the quantities so calculated can have no simple physical meaning and, in what follows, they will be written as '$\delta\Delta\Delta H^{\ddagger}$' and '$\delta\Delta\Delta S^{\ddagger}$'. It is, however, still necessary to explain why plots of '$\delta\Delta\Delta H^{\ddagger}$' *vs.* '$\delta\Delta\Delta S^{\ddagger}$', when calculated for series of related reactions, are frequently found to be linear.[4]

The explanation can be seen from the diagrammatic representation of one of these plots in Fig. 5. In the remainder of this section, the assumptions used previously in the literature will be accepted and so EF and CE will be taken to represent the limiting lines corresponding to eqns. (10) and (11), and the solid line will be taken to represent the observed results. The origin is the zero for both axes. The argument now requires an extension of FE to A and the construction of BE parallel to the $1/T$ axis.

It is obvious from Fig. 5 that the slope of EF equals $-\mathrm{BA}/\mathrm{BE}$. Similarly, the slope of CE = CB/BE. Therefore:

$$\text{(Slope of CE)} - \text{(Slope of EF)} = \frac{\mathrm{CB}}{\mathrm{BE}} + \frac{\mathrm{BA}}{\mathrm{BE}} = \frac{\mathrm{CA}}{\mathrm{BE}} \qquad (14)$$

Since EF is now taken to be a plot of eqn. (10) and CE a plot of eqn. (11), it follows that:

(*i*) $\text{(Slope of CE)} - \text{(Slope of EF)} = -\Delta\Delta H^{\ddagger}_{2}/R + \Delta\Delta H^{\ddagger}_{1}/R = {}^{\backprime}\delta\Delta\Delta H^{\ddagger\prime}/R$

(*ii*) $\mathrm{CA} = \mathrm{OA} - \mathrm{OC} = \Delta\Delta S^{\ddagger}_{1}/R - \Delta\Delta S^{\ddagger}_{2}/R = {}^{\backprime}\delta\Delta\Delta S^{\ddagger\prime}/R$

and (*iii*) $\mathrm{BE} = 1/T_{\text{inv}}$

where T_{inv} is the temperature at the maximum. Hence, from eqn. (14):

$$`\delta\Delta\Delta H^{\ddagger}\text{'}/`\delta\Delta\Delta S^{\ddagger}\text{'} = T_{\text{inv}} \qquad (15)$$

It is therefore a necessary and sufficient condition for the isoinversion relationship that the different reactions have similar values of T_{inv}. This is a direct consequence of the geometry of the plot and the definition of the terms.

Discussion

One of the main differences between this and earlier discussions[3,4] of the isoinversion relationship comes from the emphasis on the transitional region in the ln *P vs.* $1/T$ plots. The width of this transitional region cannot be exactly defined because the limiting conditions of eqns. (10) and (11) are never exactly reached. However, it is useful to consider the factors that influence the width of this region.

The obvious factor is the enthalpy difference $\Delta H^{\ddagger}_{2} - \Delta H^{\ddagger}_{3}$ for this determines the rapidity of the transition from $k_3 \gg k_2$ to $k_2 \gg k_3$ as the temperature is raised. In the reactions listed in Table 1, this quantity varies from 10 to 14 kJ mol^{-1} and, in most of the reactions listed, the corresponding entropy term $\Delta S^{\ddagger}_{2} - \Delta S^{\ddagger}_{3}$ is in the range 60–80 J K^{-1} mol^{-1}. Even with a difference of 14 kJ mol^{-1} between the enthalpies of activation, a temperature range of *ca.* 150 °C (starting from −100 °C) is needed to change from $k_3 = 10k_2$ to $k_2 = 10k_3$. Of course, a higher value of $\Delta H^{\ddagger}_{2} - \Delta H^{\ddagger}_{3}$ would decrease this temperature range but it would then be difficult to justify the compensating increase required in $\Delta S^{\ddagger}_{2} - \Delta S^{\ddagger}_{3}$ in order to make the ratio k_3/k_2 pass through unity within a conventional temperature range.

The width of the transitional region is also influenced by the fact that the activation parameters for the formation of the two diastereoisomers are not identical; hence, for the two isomers, the temperature ranges required for the transition between the two rate determining steps do not completely overlap. The transitional region in the ln *P* plot covers the overall temperature range for the changes in the rate determining steps of both diastereoisomers.

From the above arguments, it follows that the wide transitional region is not an accidental consequence of the particular parameters listed in Table 1; it is a logical necessity given the assumptions underlying Scheme 1 and eqn. (1).

The above evidence on the width and properties of the transitional region has several significant consequences as far as the interpretation of the ln *P vs.* $1/T$ plots is concerned. First, it implies that the maxima on the plots do not necessarily derive from a change in the sign of $\Delta\Delta H^{\ddagger}$ or a change from enthalpic to entropic control of the product composition. The results in Fig. 1 show that, if $\Delta\Delta H^{\ddagger}_{2}$ is negative, then a maximum can be obtained whether $\Delta\Delta H^{\ddagger}_{1}$ is positive, zero or negative.

Secondly, the evidence shows that a linear plot of ln *P vs.* $1/T$ does not necessarily indicate the magnitude of $\Delta\Delta H^{\ddagger}$. If there is only one rate determining step, the slope of the plot can be identified with $-\Delta\Delta H^{\ddagger}_{1}$ but if the system being studied is in the transitional region between two rate determining steps then a pure entropic discrimination between the diastereoisomers can give a remarkably good approximation to a straight line of finite slope, even over a range of 100 °C (Fig. 3).

The third point concerns the isoinversion relationship. When the line on one side of a maximum is recognised as coming from the transitional region, the quantities previously defined (from the slope of these lines) as $\delta\Delta\Delta H^{\ddagger}$ and $\delta\Delta\Delta S^{\ddagger}$ no longer have any simple meaning. The fact that many sets of reactions give a linear plot of $\delta\Delta\Delta H^{\ddagger}$ against $\delta\Delta\Delta S^{\ddagger}$ is however understandable from the geometrical argument leading to eqn. (15) provided that the set of reactions give similar inversion temperatures. For systems of high diastereoselectivity, the similarity of the slope of the isoinversion plots to the inversion temperature has already been noted.[4] Eqn. (15) implies that a set of reactions with widely varying inversion temperatures cannot give a linear isoinversion plot.

The above arguments have implied that a thermal reaction is being considered but many of the applications of the isoinversion relationship have come from photochemical reactions.[3,4,7,8] Scheme 1 is no longer an adquate representation of these reactions but it is still true that a highly reactive intermediate is being partitioned between different pathways in a way that depends on the temperature. There seems no reason why the above arguments concerning the transitional region should not apply also to photochemical reactions and, since all reactions of such intermediates should have low activation energies, the differences between such activation energies should be particularly small. Thus, in these examples, the transitional region should be very broad.

On the model used above, the two potentially rate determining steps occur on the same reaction path. In principle, plots of ln P *vs.* $1/T$ could also show maxima if reaction occurred through two separate reaction paths, each producing both diastereoisomers but in different ratios. If these paths are numbered 1 and 2, then the mechanistic transition occurs as k_1/k_2 changes with temperature from $k_1 \gg k_2$ to $k_1 \ll k_2$. A number of calculations have been carried out on this system and the results have a similar form to those reported above with the quantity $\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger}$ playing the same part in determining the mechanistic transition as the quantity $\Delta H_2^{\ddagger} - \Delta H_3^{\ddagger}$ does in the above calculations. Where maxima are observed in the ln P plots, it is again true that one of the intersecting lines comes from the slope in the transitional region.

In conclusion, the mechanistic implications of the above arguments are as follows. A maximum in a ln P *vs.* $1/T$ plot can still be taken as evidence of two potential rate determining stages in the reaction but only one of the lines provides valid evidence on the enthalpic and entropic discrimination involved. The two potential rate determining stages need not be on the same reaction path: the maximum can arise from competition between two separate one-stage reactions (or two separate multi-stage reactions). Conventional linear plots of the isoinversion relationship provide no additional evidence of mechanism beyond the fact that the reactions involved have similar inversion temperatures.

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