

**Some tentative explanations for the enthalpy-entropy  
compensation effect in Chemical Kinetics: From  
experimental errors to the Hinshelwood-like model**

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**Abstract** It has often been proposed that the well-known standard activation enthalpy-entropy linear plots usually found in kinetic studies for many series of homologous reactions are mere artefacts generated by the experimental errors committed in the determination of the rate constants. Here it is shown that the experimental errors can explain the existence of a standard activation enthalpy-entropy linear correlation only when the temperature obtained from the slope of that plot (compensation temperature,  $T_c$ ) is lower than or equal to the mean experimental temperature used in that study ( $T_m$ ), that is  $T_c \leq T_m$ . However, when  $T_c > T_m$  it is necessary to accept the existence of a real, physicochemically meaningful correlation between the values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  for each member of the series of reactions. Four different explanations (thermodynamic interpretation, solvent-cage effect, formation of a binding intermediate and a Hinshelwood-like model) for real enthalpy-entropy compensation effects are analysed in some detail.

**Keywords** Activation parameters · Enthalpy-entropy compensation effect · Experimental errors · Hinshelwood-like model · Isokinetic temperature

## Introduction

Arguably, the existence of an enthalpy-entropy compensation effect is the most striking experimental result that a researcher can find in the field of Chemical Kinetics. Indeed, one does not expect from a simple inspection of the law known as Arrhenius equation (although initially proposed by van't Hoff), expressing the dependence of the rate constant ( $k$ ) of a particular reaction on the absolute temperature ( $T$ ) [1]:

$$k = A e^{-\frac{E_a}{RT}} \quad (1)$$

that the pre-exponential factor  $A$  and the activation energy  $E_a$  be mutually dependent ( $R$  is the ideal-gas constant). In fact, it can be taken as certain that the mutual dependence of the two empirical parameters involved in Eq. 1 was not in the minds of van't Hoff and Arrhenius when developing their famous equation.

According to the Transition State Theory, we can also express the dependence of the rate constant on temperature by means of the Eyring equation:

$$k = \frac{k_B T}{h} (c^\circ)^{1-n} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} \quad (2)$$

where  $n$  is the kinetic order of the reaction,  $c^\circ$  is the standard-state concentration (arbitrarily taken as  $1 \text{ mol dm}^{-3}$ ),  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are the standard activation enthalpy and entropy, whereas  $k_B$  and  $h$  are the Boltzmann and Planck constants, respectively. The factor  $(c^\circ)^{1-n}$  was not initially used by Eyring but more recently it has been incorporated into the equation in

order to assure its dimensional homogeneity [2]. The relationships between the Arrhenius and Eyring parameters are straight forward:

$$E_a = \Delta H_{\ddagger}^{\circ} + RT_m \quad (3)$$

$$\ln A = \ln \left[ \frac{e k_B T_m (c^{\circ})^{1-n}}{h} \right] + \frac{\Delta S_{\ddagger}^{\circ}}{R} \quad (4)$$

where  $T_m$  is the mean of the experimental temperatures.

Thus, if we accept that, as confirmed by many experimental data reported in the published literature [3-5], there exists a linear correlation between the standard activation enthalpies and entropies for a family of related chemical reactions (differing usually either in the inert substituent of one of the reactants, provided that this is an organic species, or in the solvent used):

$$\Delta H_{\ddagger}^{\circ} = \Delta H_{\ddagger,0}^{\circ} + T_c \Delta S_{\ddagger}^{\circ} \quad (5)$$

where  $\Delta H_{\ddagger,0}^{\circ}$  (the standard activation enthalpy for a hypothetical reaction with  $\Delta S_{\ddagger}^{\circ} = 0$ ) and  $T_c$  (the compensation temperature) are the intercept and slope of the enthalpy-entropy linear plot, respectively, we must also accept (and confirmed by experimental results [6]) that there also exists a linear correlation between the Arrhenius parameters that can be expressed as:

$$E_a = E_{a,0} + RT_c \ln A \quad (6)$$

where  $E_{a,0}$  (the activation energy for a hypothetical reaction with  $A = 1 \text{ dm}^{3n-3} \text{ mol}^{1-n} \text{ s}^{-1}$ ) is the intercept of the activation energy-logarithm of the pre-exponential factor linear plot. From

Eqs. 3 and 4, it follows that the intercepts of the linear correlations shown in Eqs. 5 and 6 are related by the mathematical expression:

$$E_{a,o} = \Delta H_{\neq,o}^{\circ} + RT_m + RT_c \ln \left[ \frac{h (c^{\circ})^{n-1}}{e k_B T_m} \right] \quad (7)$$

The slopes of the linear correlations depicted in Eqs. 5 and 6 are in most cases positive ( $T_c > 0$ ). This means that there seems to exist a compensation effect so that to a certain reaction with a high value of the activation energy (or of the activation enthalpy) unfavourable to the reaction, corresponds also a high value of the pre-exponential parameter (or of the activation entropy) favourable to the reaction. This compensation effect can be studied either in the  $E_a - \ln A$  plane or in the  $\Delta H_{\neq}^{\circ} - \Delta S_{\neq}^{\circ}$  plane. The linearity of those plots leads to the conclusion that there must exist a certain temperature at which all the members of the homologous series of reactions have the same rate constant. Effectively, from Eqs. 2 and 5 this common value of the rate constant would be given by:

$$k_{iso} = \frac{k_B T_c}{h} (c^{\circ})^{1-n} e^{-\frac{\Delta H_{\neq,o}^{\circ}}{RT_c}} \quad (8)$$

We can see that the value of  $k_{iso}$  is independent of the particular member of the reaction series considered, because the values of both  $\Delta H_{\neq,o}^{\circ}$  and  $T_c$  (the intercept and slope of the linear relationship given in Eq. 5) involved in Eq. 8 are constant for the homologous series of reactions. However, the occurrence of  $\Delta H_{\neq}^{\circ}$  vs.  $\Delta S_{\neq}^{\circ}$  or  $E_a$  vs.  $\ln A$  linear plots does not warrant the existence of a common value of the rate constant ( $k_{iso}$ ) for the family of reactions, since (as will be shown later) the compensation effect might sometimes be just an artefact

resulting from experimental errors in the determination of the activation parameters. When the value of  $k_{\text{iso}}$  does exist, the compensation temperature is also called the isokinetic temperature for the homologous series of reactions ( $T_c = T_i$ ).

Several proposals have been made to account for these theoretically unexpected experimental results, but a single explanation accepted by most researchers remains so far elusive. Nevertheless, we can safely state that the basis of the Chemical Kinetics field will not be complete until the existence of experimental standard activation enthalpy-entropy linear correlations and the physicochemical meaning of isokinetic temperatures are satisfactorily explained. Some attempts to advance further in that objective are developed in the following sections of this article.

## **Results and discussion**

In this section, different possible explanations for the enthalpy-entropy compensation effect will be studied in detail. The list of proposals considered hereafter does not try to be exhaustive, but only illustrative of the complexity of the problem analysed. Other plausible theoretical approximations have already been published by other authors [7-21].

### *Experimental errors*

It has been shown that the accidental experimental errors associated to the rate constants determined at different temperatures lead to errors in the values of the activation enthalpy and entropy that are mutually interdependent [22, 23]. Thus, the accidental errors in the activation enthalpy and entropy always are of the same sign, and the higher the error associated to the

activation enthalpy the higher the error associated to the activation entropy. Moreover, it can be demonstrated that these interdependent errors lead to  $\Delta H_{\ddagger}^{\circ}$  vs.  $\Delta S_{\ddagger}^{\circ}$  linear plots with slopes very close to the mean of the experimental temperatures.

In Fig. 1 an example of this kind of behaviour is shown. To generate the plot, it has been assumed that the kinetics of a single reaction with the typical activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$  has been studied at five temperatures in the range 15-35 °C, and that the rate constants at those temperatures have been determined 20 times with a different set of evenly distributed random errors each time. The same calculations were repeated for the experimental temperature ranges 40-60 °C and 65-85 °C. We can see (Table 1) that, in the three cases, the compensation temperature obtained from the slope of the plot exactly matches the mean of the experimental temperatures corresponding to that plot ( $T_c = T_m$ ), as theoretically predicted by statistical models [24-26]. It is interesting to notice that in many of the enthalpy-entropy linear correlations reported in the literature there is also a close convergence between the temperatures  $T_c$  (obtained experimentally from each plot) and  $T_m$  (arbitrarily chosen by the researchers) [27].

A second example has been analysed. In this case, it has been assumed that the kinetics of a set of 50 different reactions, with values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  mutually independent and randomly scattered with divergences within the range of  $\pm 2.5\%$  with respect to the mean values of the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$  (Fig. 2, top), has been studied in the temperature range 15-35 °C, again with evenly distributed random errors within the range of  $\pm 10\%$  in the determination of the rate constants, leading to a standard activation enthalpy-entropy linear correlation (Fig. 2, bottom) but with  $T_c < T_m$  (Table 1).

Finally, a third example has been analysed whose only difference with respect to the former case is that the random divergences of the activation parameters with respect to the mean values for the set of 50 reactions are now within the range of  $\pm 5\%$  (Fig. 3, top), but keeping the evenly distributed random errors of the rate constants within the range of  $\pm 10\%$ . An acceptable standard activation enthalpy-entropy linear correlation was also obtained in this case (Fig. 3, bottom) and again it is fulfilled that  $T_c < T_m$  (Table 1).

We can see that for a single reaction the existence of evenly distributed random errors in the rate constants led to a standard activation enthalpy-entropy linear plot with  $T_c = T_m$ . For a set of reactions with values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  mutually independent (scattered) the experimental errors in the rate constants led also to a standard activation enthalpy-entropy linear plot but this time with  $T_c < T_m$ . Moreover, the higher the divergences between the activation parameters for the series of reactions the lower will be the value of  $T_c$  with respect to  $T_m$  (compare the values of  $T_c$  corresponding to the last two rows in Table 1).

This result could be easily anticipated considering that for a set of reactions with scattered, mutually independent values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  the slope of an activation enthalpy-entropy linear plot is naturally close to zero (see Fig. 2, top and Fig. 3, top). If we incorporate now an artificial correlation between the values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  for the series of reactions caused by the experimental errors in the activation enthalpy and in the activation entropy (that are mutually dependent on each other), the slope of the enthalpy-entropy linear plot will be intermediary between those corresponding to the real, scattered values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  (in the absence of errors, slope = 0, Figs. 2, top and 3, top) and to the linearly correlated values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  induced by experimental errors (slope =  $T_c = T_m$ , Fig. 1), thus leading to a compensation temperature  $T_c < T_m$  (Figs. 2, bottom and 3, bottom).



The data given in Table 1 and obtained from the linear plots shown in Figs. 1-3 can be generalized stating the following law: The experimental errors committed in the determination of the rate constants can explain the existence of a standard activation enthalpy-entropy linear correlation only when the temperature obtained from the slope of that plot is lower than or equal to the mean experimental temperature used in that study ( $T_c \leq T_m$ ). Moreover, since the accidental errors in the activation enthalpy and entropy always are of the same sign (either both positive or both negative), they can only lead to positive values of the compensation temperature:  $0 < T_c \leq T_m$ . It should be emphasized, though, that this law does not necessarily mean that all the  $\Delta H_{\ddagger}^{\circ}$  vs.  $\Delta S_{\ddagger}^{\circ}$  linear plots with  $T_c \leq T_m$  are artefacts generated by the experimental errors, only that in these cases the experimental-error explanation should be regarded as a rational alternative. Because of this, some authors have discussed the possibility that all the enthalpy-entropy compensation effects reported in the literature through the years be merely a phantom phenomenon caused by the experimental errors [28-30].

However, there exist some examples in the published literature of standard activation enthalpy-entropy linear correlations leading to values with distinctly  $T_c > T_m$ . For instance, we can analyse the results reported for the oxidation of a series of substituted cinnamic acids by *N,N*-dibutyl-*N*-methylbutylammonium permanganate in dichloromethane solutions studied in the temperature range 0.0-25.0 °C [31]. In this case, a standard activation enthalpy-entropy linear correlation is obtained with  $T_c = 627 \pm 52$  K (much higher than  $T_m = 286$  K) and  $r = 0.96438$  (Fig. 4).

We can conclude that, at least in the cases when  $T_c > T_m$ , it is necessary to invoke the existence of a real, physicochemically meaningful correlation between the values of  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$  for each member of the series of reactions, since the experimental errors cannot account

for a correlation of this type. In the following subsections we will analyse some possible explanations.

#### *The thermodynamic interpretation*

A simple thermodynamic interpretation of the enthalpy-entropy compensation effect is possible if we take into consideration that most elementary reactions involve either the formation of new chemical bonds or the breaking of formerly existing chemical bonds or both. The formation of chemical bonds in the activation process is expected to contribute negatively to the value of  $\Delta H_{\ddagger}^{\circ}$  indeed, but also to the value of  $\Delta S_{\ddagger}^{\circ}$ , since a strongly-bonded activated complex is more stable (less energetic) and more ordered (less entropic) than a loosely-bonded one. On the contrary, the breaking of chemical bonds in the activation process is expected to contribute positively to the values of both  $\Delta H_{\ddagger}^{\circ}$  and  $\Delta S_{\ddagger}^{\circ}$ . Hence, on the basis of purely thermodynamic considerations, it seems clear that some kind of enthalpy-entropy compensation might exist.

Given that the same argument can be applied to the thermodynamic  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  parameters of a reaction, a similar compensation effect would be expected in this case. Actually, some examples have been reported where measurement of the equilibrium constants of a homologous series of reactions at different temperatures leads to standard reaction enthalpy-entropy compensation correlations. In fact, a thermodynamic isoequilibrium relationship can be directly deduced from kinetic considerations if isokinetic relationships with equal or similar slopes are associated to both the forward and reverse rate constants involved in the equilibrium [32]. However, there are many other examples reported where no enthalpy-entropy compensation effect is associated with the equilibrium constants for a series of related reactions. For instance, we can see in Fig. 5 that a rather scattered  $\Delta H^{\circ}$  vs.  $\Delta S^{\circ}$

plot ( $r = 0.36542$ ) is obtained for the dissociation reactions of a series of substituted anilinium ions in aqueous solutions [33]. Moreover, the negative value of the slope ( $T_c = -303 \pm 187$  K) indicates that an enthalpy-entropy anti-compensation effect (rather than an enthalpy-entropy compensation one) is present in this case. Thus, it seems that, in cases such as this, a compensation effect is not found in the equilibrium constant because either at least one of the two rate constants (forward and reverse) involved does not present any kinetic compensation effect or, else, the two isokinetic temperatures are very different. We can also conclude that considerations of a purely thermodynamic nature might not be enough to explain the enthalpy-entropy compensation effect usually found in Chemical Kinetics, and that a genuinely kinetic interpretation might be necessary.

#### *The solvent-cage effect*

In the case of elementary bimolecular reactions performed in solution, a compensation between the Arrhenius pre-exponential factor and the activation energy for each member of a series of homologous reactions could be predicted from the existence of the solvent-cage effect, according to which, after their first collision, the two reactant molecules are trapped inside a cage whose walls are formed by the solvent molecules, so that if the first collision is not efficient for the reaction to take place (because of a bad orientation or a too low energy) new collisions with different orientation and energy are possible before the reactant molecules leave the solvent cage. If we consider that, following the collision theory for elementary bimolecular reactions, the Arrhenius pre-exponential factor is directly proportional to the frequency of collisions between the reactant molecules per volume unit, we can rewrite the Arrhenius equation for bimolecular reactions in aqueous solution as:

$$k = \alpha_{\text{sc}}(E_a, T) A' e^{-\frac{E_a}{RT}} \quad (9)$$

where  $\alpha_{\text{sc}}(E_a, T)$  is the average number of collisions experienced by the reactant molecules inside the solvent cage after their first encounter. Given that an increase of  $E_a$  (from one member of the reaction series to another) or a decrease of temperature both lead to a decrease in the probability of each collision to be reactive, and so to an increase in the time of residence of the reactant molecules inside the solvent cage leading to an increase in the average number of collisions per encounter, it is clear that parameter  $\alpha_{\text{sc}}(E_a, T)$  increases with increasing  $E_a$  and decreases with increasing  $T$ . Hence, a compensation effect is predicted according to this explanation, since the Arrhenius pre-exponential factor would be now  $A = \alpha_{\text{sc}}(E_a, T) A'$  and would increase when the activation energy increases from a member of the homologous reaction series to another. Thus, according to this model, the enthalpy-entropy compensation effect would be caused by the fact that an increase in the activation energy would be partially compensated by an increase in the number of collisions of the reactant molecules when they become trapped inside a solvent cage after their first encounter.

However, because of the lack of a mathematical model expressing the dependence of the function  $\alpha_{\text{sc}}(E_a, T)$  on the independent variables  $E_a$  and  $T$ , this explanation for the enthalpy-entropy compensation effect cannot be analyzed further from a theoretical point of view. An experimental confirmation or dismissal of this proposal is possible in principle if we take into consideration that stirring of the solution should have a pronounced effect on the value of  $\alpha_{\text{sc}}(E_a, T)$ . Since an increase in the stirring rate is expected to provoke a decrease in the contribution of the solvent-cage effect, it should also provoke a progressive disappearance

of the standard activation enthalpy-entropy compensation effect, provided that the solvent-cage interpretation of it be correct.

*Formation of a binding intermediate*

Most elementary reactions are indeed of the bimolecular type:



We can assume as a working hypothesis what is widely accepted for unimolecular reactions in the gas phase, that bimolecular reactions might not be elementary after all either but composed by a sequence of two truly elementary steps, including in this case the formation of a binding intermediate between the two reactants:



Now, if we assume that the binding intermediate is in steady state, the rate law obtained for the reaction is:

$$v = \frac{k_1 k_2}{k_{-1} + k_2} [A] [B] \quad (13)$$

and the observed rate constant can be expressed as:

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} + k_2} = \frac{k_1}{1 + \frac{k_{-1}}{k_2}} \quad (14)$$

Application of the steady-state approximation to the assumed binding intermediate requires as the only condition that the forward process in the reaction depicted in Eq. 11 be slow enough in comparison with the backward process in the same reaction and the reaction depicted in Eq. 12 globally considered. This must be so because this approximation can be applied only to intermediates present in minute concentrations with respect to the initial concentration of the limiting reactant. Since, according to this approximation, the total rate of decay of the intermediate equals its rate of formation, the latter condition must be understood in terms of rate constants rather than in terms of reaction rates and, taking into consideration the limitations imposed on the units of the magnitudes to be compared by the principle of dimensional homogeneity, the condition can be expressed as  $k_1 [B]_0 \ll k_{-1} + k_2$  (assuming that A is the limiting reactant, that is  $[B]_0 > [A]_0$ ). We can thus see that the steady-state condition is compatible with any value of the  $k_{-1}/k_2$  ratio, and this consideration will be important below when this model is checked out from a numerical point of view.

On the other hand, application of the Arrhenius equation to the rate constants of the three elementary reactions involved leads to:

$$k_{\text{obs}} = \frac{A_1 e^{-\frac{E_{a,1}}{RT}}}{1 + \frac{A_{-1} e^{-\frac{E_{a,-1}}{RT}}}{A_2 e^{-\frac{E_{a,2}}{RT}}}} = \frac{A_1 e^{-\frac{E_{a,1}}{RT}}}{1 + \frac{A_{-1}}{A_2} e^{-\frac{(E_{a,-1} - E_{a,2})}{RT}}} = \frac{A_1 e^{-\frac{E_{a,1}}{RT}}}{1 + Q_A e^{\frac{\Delta E_a}{RT}}} \quad (15)$$

where  $Q_A = A_{-1}/A_2$  and  $\Delta E_a = E_{a,2} - E_{a,-1}$ .

For a series of related reactions, the main difference between its members is expected to be in the activation energy ( $E_{a,2}$ ) associated to the formation of products (Eq. 12), whereas the activation energies associated to the forward reactions ( $E_{a,1}$ ) corresponding to the formation of the intermediate (Eq. 11), as well as those associated to the respective reverse reactions ( $E_{a,-1}$ ), are expected to be very similar for the diverse members of the series. Moreover, and for the same reason, a positive value of  $\Delta E_a$  for each reaction of the homologous series is more probable than a negative one ( $E_{a,2} > E_{a,-1}$ ). Assuming as an example the values  $A_1 = 1.15 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_{a,1} = 50 \text{ kJ mol}^{-1}$ ,  $Q_A = 1.77 \times 10^{-2}$  and  $\Delta E_a = 10 \text{ kJ mol}^{-1}$  excellent results were obtained for the binding-intermediate model. As indicated above, these values are perfectly consistent with the hypothesis of the binding intermediate being in steady state, because the values of the rate constants  $k_{-1}$  and  $k_2$  are not required for the calculations, but only those of  $k_1$  and the ratio  $k_{-1}/k_2$ . In the first place, both the Arrhenius (Fig. 6, top,  $r = 0.9999945$ ) and Eyring (Fig. 6, bottom,  $r = 0.9999903$ ) plots obtained for the binding-intermediate model led to surprisingly good linear correlations in the temperature range 20-60 °C. We can conclude that, although the existence of a sum in the denominator of Eq. 15 implies the presence of a certain curvature in both the Arrhenius and Eyring plots, it is in typical cases too small to be detected and would probably be masked by the experimental errors. Moreover, from the Eyring plots obtained in the range  $\Delta E_a = 0\text{-}10 \text{ kJ mol}^{-1}$  (with increments of  $1 \text{ kJ mol}^{-1}$ ), the standard activation enthalpy-entropy linear plot obtained for the binding-intermediate model yielded an excellent straight line (Fig. 7,  $r = 0.99955$ ) with a compensation temperature significantly higher than the mean experimental temperature ( $T_c = 469 \pm 5 \text{ K} > T_m = 313 \text{ K}$ ).

*The Hinshelwood-like model*

This theoretical model was initially proposed for unimolecular reactions in the gas phase. Interestingly enough, it leads to an expression for the rate constant according to which the Arrhenius pre-exponential parameter depends on (and increases with) the activation energy of the reaction [34]. It may be proposed, in principle, its generalization to all types of elementary reactions, both unimolecular and bimolecular, either in the gas phase or in solution, the corresponding rate constants being then given by the equation:

$$k = A'' \left( \frac{E_a}{RT} \right)^{s-1} e^{-\frac{E_a}{RT}} \quad (16)$$

where  $s$  can be taken as the number of different vibrational modes of the activated complex. This model is thus based on the consideration of the distribution of internal energy between the different vibrational modes of the activated complex. We can see that for values of  $s > 1$  a compensation effect is straightforwardly predicted from the mathematical form of Eq. 16, since if the activation energy increases from one member of the homologous series to another (unfavourable to the reaction), the same will happen with the pre-exponential factor (favourable to the reaction).

Assuming as an example the values  $A'' = 3.69 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_a = 100 \text{ kJ mol}^{-1}$  and  $s = 9$  both the Arrhenius (Fig. 8, top,  $r = 0.999988$ ) and Eyring (Fig. 8, bottom,  $r = 0.999983$ ) plots obtained for the Hinshelwood-like model (as found also above for the binding-intermediate model) led to excellent linear correlations in the temperature range 20-60 °C. From the Eyring plots obtained in the range  $E_a = 100\text{-}150 \text{ kJ mol}^{-1}$  (with increments of 5 kJ mol<sup>-1</sup>), the standard activation enthalpy-entropy linear plot obtained for the Hinshelwood-like model yielded a reasonably good straight line (Fig. 9,  $r = 0.99840$ ) with a compensation temperature much higher than the mean experimental temperature ( $T_c = 1855 \pm 35 \text{ K} > T_m =$



313 K). Although a very slight upward-concave curvature can be observed in the plot, in a real case it would probably pass unnoticed because of the experimental errors.

#### *Comparison between models*

The fact that experimental errors in the determination of the activation parameters can explain the existence of enthalpy-entropy compensation plots under certain particular circumstances has already been addressed in the literature [22-26]. The new contribution from the present work in relation to this problem is that for an homologous series of reactions with equally dispersed activation enthalpies and entropies the experimental errors can only lead to compensation temperatures below the mean experimental temperature ( $T_c \leq T_m$ ).

On the other hand, among the different tentative explanations proposed here for the real standard activation enthalpy-entropy linear relationships, both the thermodynamic interpretation and the solvent-cage effect have the disadvantage of offering (at least for the time being) only qualitative predictions of the kinetic compensation effect. On the contrary, both the binding-intermediate and Hinshelwood-like models are capable of offering quantitative explanations.

The latter model seems to lead to values of the compensation temperature much higher than the mean experimental temperature ( $T_c \gg T_m$ ), although in most of the experimental results reported in the literature the value of  $T_c$  is close to that of  $T_m$ . Actually, an equation mathematically equivalent to Eq. 16 has already been considered for the analysis of the isokinetic relationship in the reaction of *p*-fluoronitrobenzene and azide ion performed in a series of different solvents, obtaining a good agreement between experimental and calculated activation entropies, although the compensation temperature for that reaction series was rather high ( $T_c = 1724$  K) [35]. In order to decrease the difference  $T_c - T_m$ , the Hinshelwood-like

model would require a very high value of parameter  $s$ . However, as we can infer from Eq. 16, this would result in a strong (inverse) dependence of the pre-exponential factor on temperature, leading to very pronounced deviations of the experimental data from the linear relationships predicted by both the Arrhenius and Eyring equations, deviations that are not observed for lower values of parameter  $s$  (Fig. 8).

Thus, of the four theoretical interpretations presented in this work for the real kinetic enthalpy-entropy compensation effect, it is the binding-intermediate model the one that can be selected as the best choice to explain the experimental data. According to this proposal, the physical meaning that can be attributed to parameter  $T_c$  at the molecular level is related to the values of the activation energies associated to rate constants  $k_1$  and  $k_2$ . For instance, if the compensation temperature is higher than the mean experimental temperature ( $T_c > T_m$ ) it must be concluded that for most members of the homologous series of reactions it is fulfilled that  $E_{a,2} > E_{a,1}$ . On the contrary, if  $T_c < T_m$  it must be concluded that  $E_{a,2} < E_{a,1}$ . In this way,  $T_c$  can be interpreted as a temperature high enough ( $\Delta E_a > 0$ ) or low enough ( $\Delta E_a < 0$ ) so that  $k_2 \gg k_1$ . The resulting compensation effect can be immediately inferred from Eq. 14 provided that the value of rate constant  $k_1$  be approximately the same for all the members of the reaction series.

In addition, the equation serving as mathematical base for the binding-intermediate model (Eq. 15) can be regarded as a generalization of the Arrhenius equation (Eq. 1). Effectively, Eq. 15 can be reduced to Eq. 1 under three different situations: (i)  $\Delta E_a = 0$ , (ii)  $Q_A e^{\frac{\Delta E_a}{RT}} \ll 1$ , and (iii)  $Q_A e^{\frac{\Delta E_a}{RT}} \gg 1$ , the observed activation energy being  $E_{a,obs} = E_{a,1}$  in the first two cases and  $E_{a,obs} = E_{a,1} + \Delta E_a$  in the third case. Thus, Eq. 15 is consistent with the kinetic behavior found for the majority of the reactions, for which the  $\ln k_{obs}$  vs.  $1/T$  plots lead to straight lines. Moreover, Eq. 15 can potentially explain certain

deviations from the standard behavior, either when the Arrhenius plot shows an upward-concave curvature [36] or a downward-concave curvature [37]. According to Eq. 15 these two different deviations from the Arrhenius behavior would be caused by the two possible signs of the  $\Delta E_a$  parameter ( $\Delta E_a < 0$  in the first case and  $\Delta E_a > 0$  in the second).

## Conclusions

The existence of evenly distributed random errors committed in the determination of the rate constants at different temperatures can explain the finding of standard activation enthalpy-entropy linear plots, but only when the compensation temperature is lower than or equal to the mean experimental temperature used in the study ( $T_c \leq T_m$ ). However, some theoretical interpretations, such as the binding-intermediate model or the Hinshelwood-like model, can explain the kinetic enthalpy-entropy compensation plots found with  $T_c > T_m$ . Of the different theoretical interpretations proposed in the present work for the real kinetic enthalpy-entropy compensation effect (not caused by experimental errors), the binding-intermediate model seems to stand out as the best choice to explain the experimental data. Additionally, this model can account for deviations of the Arrhenius law observed in certain particular reactions.

## Methods

The simulation of experimental errors associated to the rate constants corresponding to different temperatures required for the calculations involved in this work, as well as the two sets of mutually independent standard activation enthalpies and entropies for two homologous series of reactions, were obtained with the aid of a computerized generator of random numbers (Kaleidagraph) within the limits from  $-10\%$  to  $+10\%$  for the rate constants (Fig. 1, Fig. 2, bottom and Fig. 3, bottom), and from  $-2.5\%$  to  $+2.5\%$  (Fig. 2, top) and from  $-5\%$  to  $+5\%$  (Fig. 3, top) for the activation parameters. Different sets of evenly distributed random errors in the rate constants (or of evenly distributed random activation parameters) were generated with that program. It was checked that the mean value of the accidental errors approached zero. For instance, for 100 errors with absolute value  $< 10\%$  the mean was 0.0494, what represents less than 0.5% of the maximum value considered. Normal least-square linear regressions were employed in the determination of the compensation temperatures ( $T_c$ ), all the pseudo-experimental points being equally weighted.

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**Table 1** Statistical data for the standard activation enthalpy-entropy compensation plots generated by experimental errors <sup>a</sup>

$T_m^b$ (K)	$T_c^c$ (K)	$r^d$
298 <sup>e</sup>	298	0.99959
323 <sup>e</sup>	323	0.99966
348 <sup>e</sup>	348	0.99970
298 <sup>f</sup>	277	0.94835
298 <sup>g</sup>	237	0.84155

<sup>a</sup> Accidental errors of up to  $\pm 10\%$  in the determination of the rate constants

<sup>b</sup> Mean experimental temperature

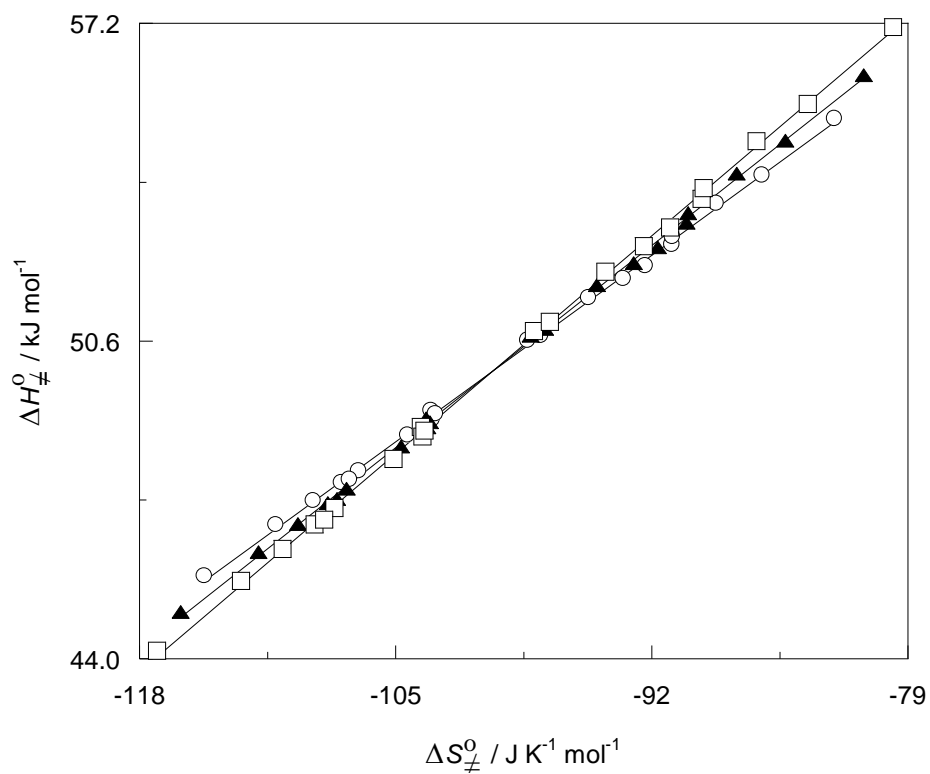
<sup>c</sup> Compensation temperature

<sup>d</sup> Linear correlation coefficient

<sup>e</sup> For a single reaction with the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$

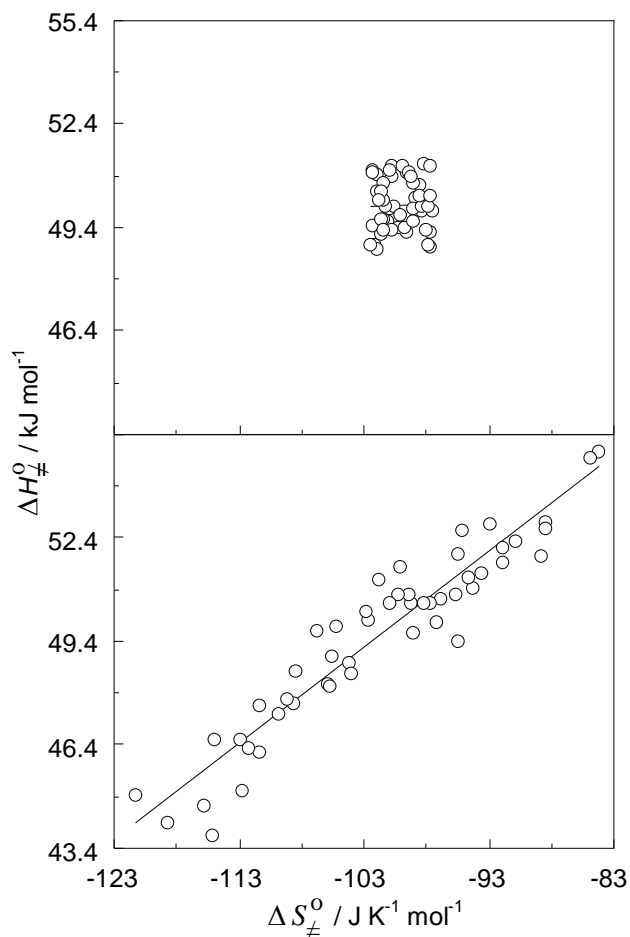
<sup>f</sup> For a series of 50 reactions with random divergences of up to  $\pm 2.5\%$  with respect to the mean values of the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>g</sup> For a series of 50 reactions with random divergences of up to  $\pm 5\%$  with respect to the mean values of the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$

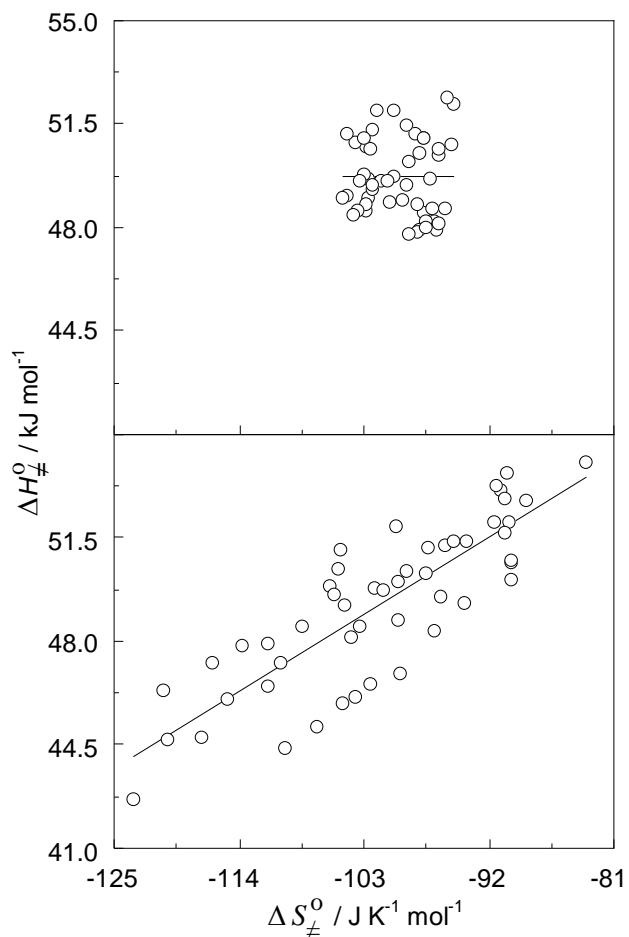


**Fig. 1** Standard activation enthalpy-entropy linear correlations as artefacts generated by accidental errors of up to  $\pm 10\%$  in the determination of the rate constants for a single reaction with the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$  studied at the mean experimental temperatures 25.0 (circles), 50.0 (triangles) and 75.0 (squares)  $^{\circ}\text{C}$

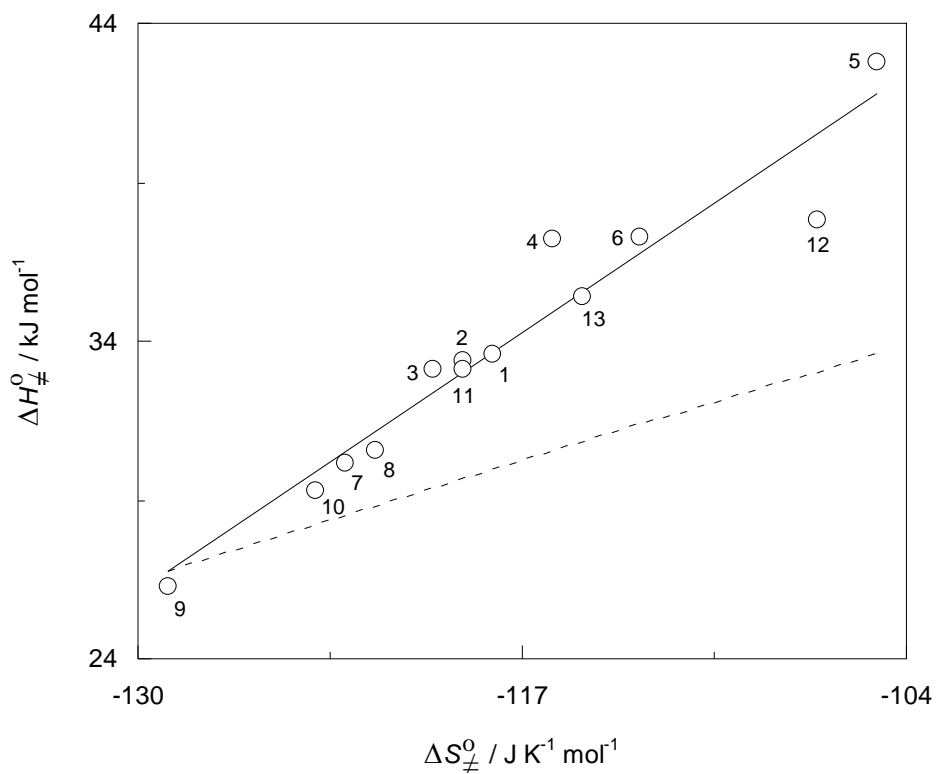




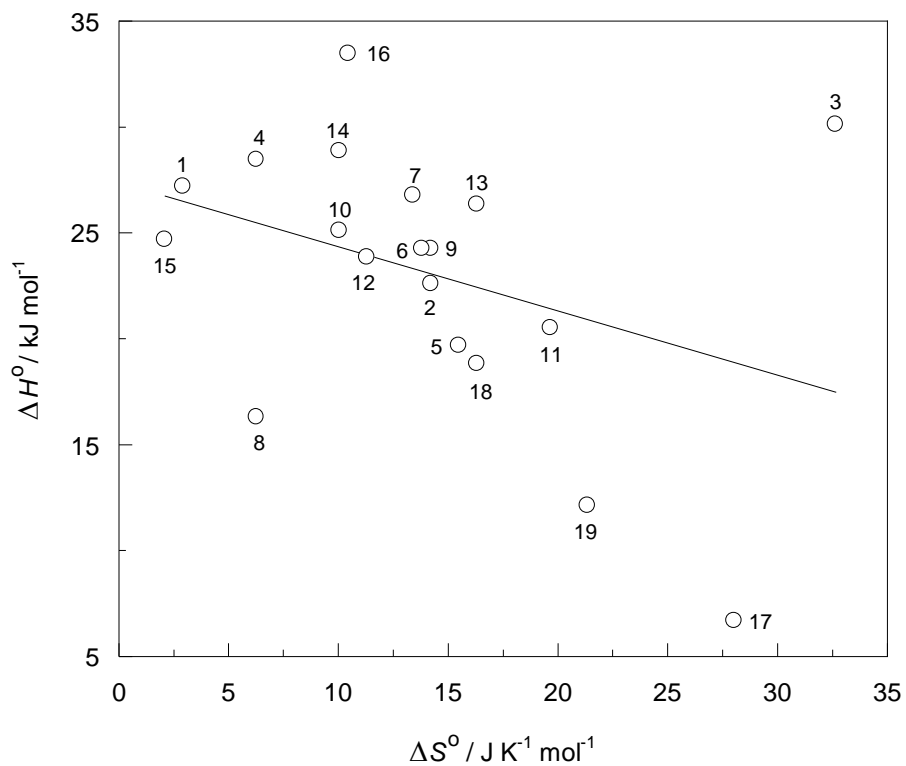
**Fig. 2** Standard activation enthalpy-entropy linear correlation (bottom) as an artefact generated by accidental errors of up to  $\pm 10\%$  in the determination of the rate constants for a series of 50 reactions (top) with random divergences of up to  $\pm 2.5\%$  with respect to the mean values of the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{ mol}^{-1}$  studied at the mean experimental temperature of  $25.0 \text{ }^{\circ}\text{C}$



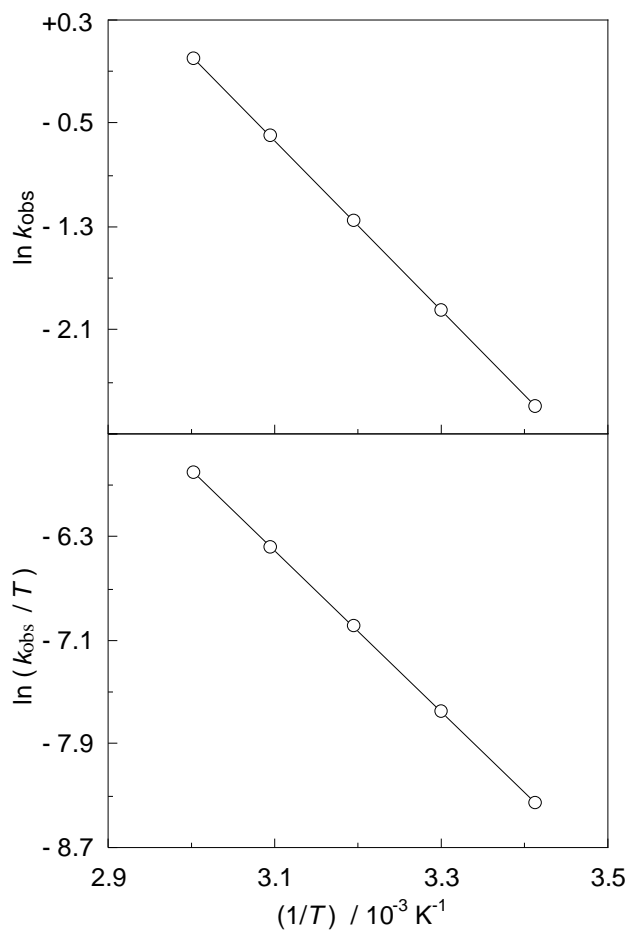
**Fig. 3** Standard activation enthalpy-entropy linear correlation (bottom) as an artefact generated by accidental errors of up to  $\pm 10\%$  in the determination of the rate constants for a series of 50 reactions (top) with random divergences of up to  $\pm 5\%$  with respect to the mean values of the activation parameters  $\Delta H_{\ddagger}^{\circ} = 50 \text{ kJ mol}^{-1}$  and  $\Delta S_{\ddagger}^{\circ} = -100 \text{ J K}^{-1} \text{mol}^{-1}$  studied at the mean experimental temperature of  $25.0 \text{ }^{\circ}\text{C}$



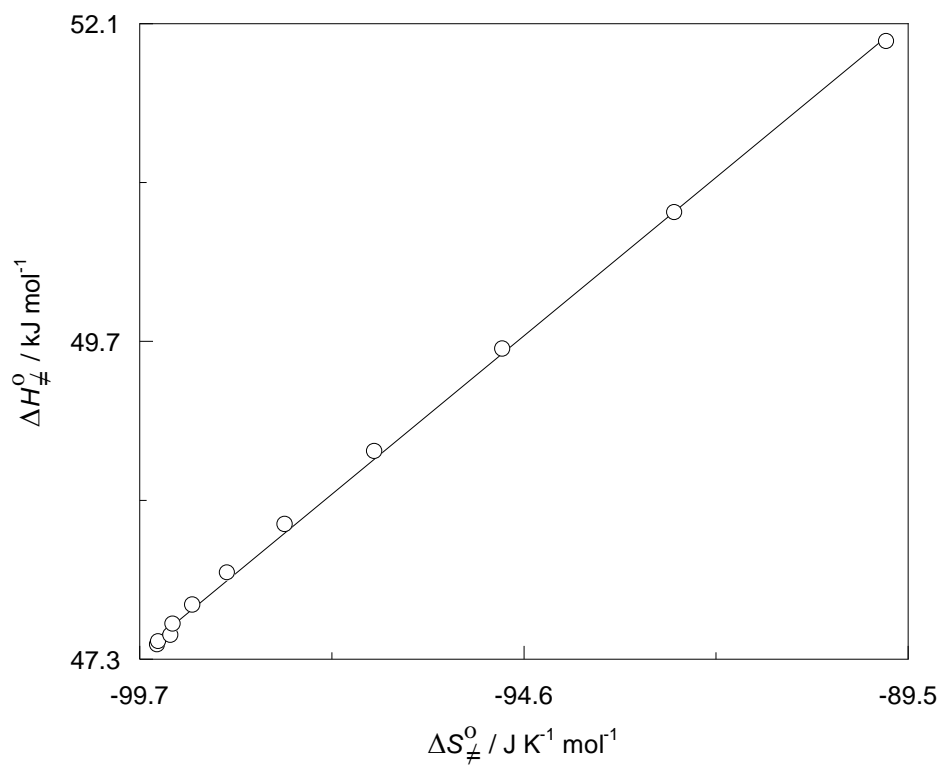
**Fig. 4** Standard activation enthalpy-entropy linear correlation for the oxidation of a series of substituted cinnamic acids by *N,N*-dibutyl-*N*-methylbutylammonium permanganate in dichloromethane solutions studied in the temperature range 0.0-25.0 °C. Substituents: None (1),  $\alpha$ -D (2),  $\beta$ -D (3),  $\alpha$ -CH<sub>3</sub> (4),  $\alpha$ -C<sub>6</sub>H<sub>5</sub> (5), *o*-OCH<sub>3</sub> (6), *m*-Cl (7), *m*-Br (8), *m*-NO<sub>2</sub> (9), *m*-CF<sub>3</sub> (10), *m*-OCH<sub>3</sub> (11), *p*-OCH<sub>3</sub> (12) and *p*-CH<sub>3</sub> (13). The dashed line corresponds to a linear correlation with slope =  $T_m = 286$  K



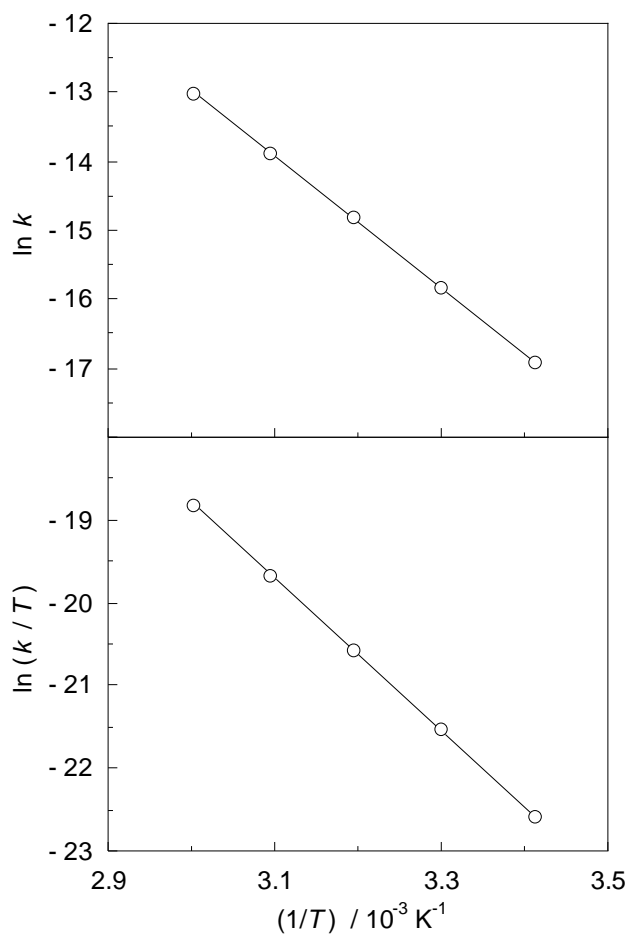
**Fig. 5** Standard reaction enthalpy-entropy linear correlation for the dissociation of a series of substituted anilinium ions in aqueous. Substituents: None (1), *o*-F (2), *m*-F (3), *p*-F (4), *o*-Cl (5), *m*-Cl (6), *p*-Cl (7), *o*-Br (8), *m*-Br (9), *p*-Br (10), *o*-I (11), *m*-I (12), *p*-I (13), *o*-OCH<sub>3</sub> (14), *m*-OCH<sub>3</sub> (15), *p*-OCH<sub>3</sub> (16), *o*-NO<sub>2</sub> (17), *m*-NO<sub>2</sub> (18) and *p*-NO<sub>2</sub> (19)



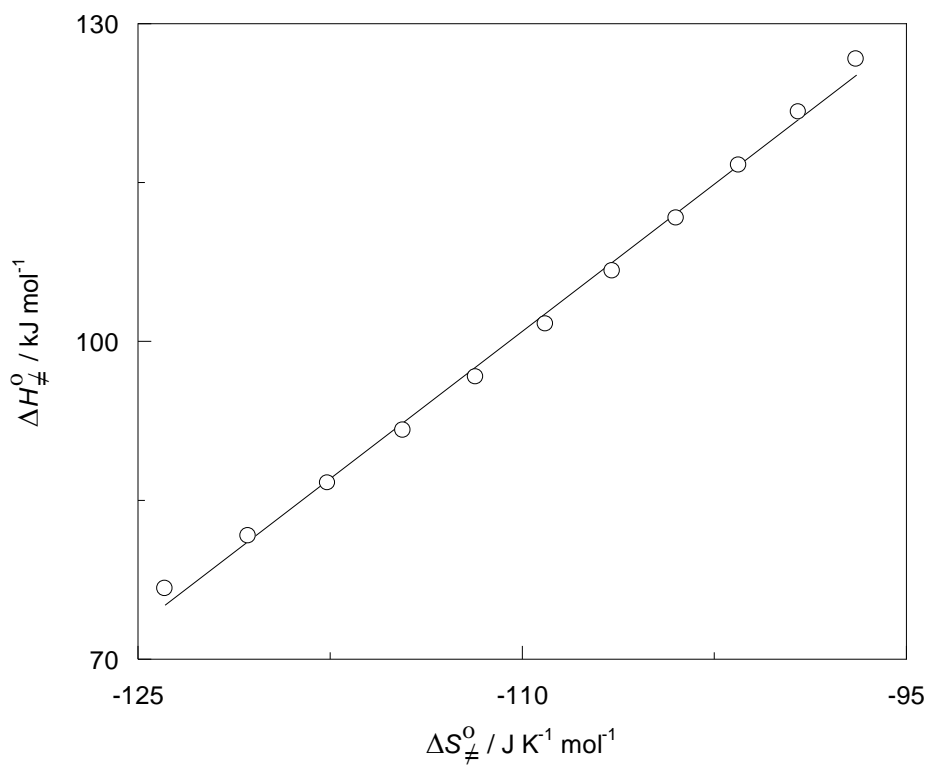
**Fig. 6** Arrhenius (top) and Eyring (bottom) linear plots for the binding-intermediate model with  $A_1 = 1.15 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_{a,1} = 50 \text{ kJ mol}^{-1}$ ,  $Q_A = 1.77 \times 10^{-2}$  and  $\Delta E_a = 10 \text{ kJ mol}^{-1}$  in the temperature range 20-60 °C



**Fig. 7** Standard activation enthalpy-entropy linear plot for the binding-intermediate model with  $A_1 = 1.15 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_{a,1} = 50 \text{ kJ mol}^{-1}$ ,  $Q_A = 1.77 \times 10^{-2}$  and  $\Delta E_a = 0\text{-}10 \text{ kJ mol}^{-1}$  (with increments of  $1 \text{ kJ mol}^{-1}$ ) in the temperature range  $20\text{-}60 \text{ }^{\circ}\text{C}$



**Fig. 8** Arrhenius (top) and Eyring (bottom) linear plots for the Hinshelwood-like model with  $A'' = 3.69 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_a = 100 \text{ kJ mol}^{-1}$  and  $s = 9$  in the temperature range 20-60 °C



**Fig. 9** Standard activation enthalpy-entropy linear plot for the Hinshelwood-like model with  $A'' = 3.69 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_a = 100\text{-}150 \text{ kJ mol}^{-1}$  (with increments of  $5 \text{ kJ mol}^{-1}$ ) and  $s = 9$  in the temperature range  $20\text{-}60 \text{ }^\circ\text{C}$