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On transient species and activation energies in heterogeneous catalysis

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A discussion is presented on the relation between true and apparent activation energies found in heterogeneous catalysis. The possibility of a transient species defining the rate determining step is emphasized. In such a case, the difference between apparent and true activation energies can be quite small. Such a condition is of importance for the understanding of phenomena involving the activation energy, such as the isokinetic effect.

Keywords: energy of activation; heat of adsorption; isokinetic temperature; transient species; precursors

1. Introduction

The use of information from activation energies determined in heterogeneous catalysis has for a long time been in disrepute. The reason for this is that the experimental values (E_{exp}) are not representing the theoretically relevant activation energies (E) but may appear of quite different magnitudes. The difference between these concepts are caused (vide e.g. Laidler [1]) by the existence of equilibria of reactants (or reactant and catalyst) before the rate determining step. These equilibria can be quite complicated as, e.g., those proposed for describing the hydrogenolysis of alkanes [2].

Nevertheless, activation energies are part of many effects that – unless they are mere artefacts – must be quantitatively understood. This has been thoroughly discussed recently by Bond [3]. One such effect is the isokinetic effect or compensation effect meaning [4] that the Arrhenius lines for a series of similar but slightly different systems intersect in one and the same point, at one and the same temperature, the isokinetic temperature, T_{iso}. A classical example of this effect is the work by Cremer and associates on the catalytic decomposition of formic acid [5]. Such a common point of intersection implies that there is a linear relation between $\ln k_0$ and the experimental activation energy E_a, where k_0 is the preexponential factor.

Another effect of possible interest has been pointed out [6] by the present author, viz., that in some occasions there seems to be a stepwise change of the experimentally determined energy of activation. It was found that the size of the increment was such that it corresponded to a vibrational energy quantum of that molecular vibration mode that most likely would take the molecule towards reaction.

We are now facing a dilemma. E.g. for the simple example to be discussed below, it is known [1] that

$$E_{\text{exp}} = E - Q_a \,, \qquad (1)$$

where Q_a means the heat of adsorption. A regular increment, ΔE_{exp}, can be found only if the heat of adsorption is constant. If furthermore a proportionality exists between E_{exp} and the increment ΔE_{exp}, as is sometimes found [7], the additional condition holds that $Q_a = 0$. The dilemma arises from the present paradigm that the adsorption is essential for the molecule to be reactive. Hence Q_a cannot be equal to zero and it is rather improbable that it is constant for different conditions.

The dilemma is strengthened by the attempts made to describe the origin of the isokinetic effect. It is now a common view [8–10], although the details in the description differ, that the effect is caused by interaction between vibrations of the reactant and vibrations corresponding to the energy of the "heat bath", e.g. the catalyst or the solvent. In these attempts, however, the energy of activation entering the expressions is the true one, E, whereas the experimental compensation effect is found for the apparent value, E_a.

Recently it was suggested by the present author [11] that the isokinetic effect could be used to predict the mechanism of the reaction or at least the nature of the rate determining step. But in using this information to describe the observed kinetics dependence of concentrations of the reactants he also constructed [12] a complicated but conventional scheme of reactions which undoubtedly will cause $E_a \neq E$. Unless one evokes some sort of complementarity principle, these two approaches are not coherent.

The aim of the present paper is to use the concepts of "precursors" and "transient states" as introduced by Roberts [13]. The transient for short, is thought of to be a just very lightly adsorbed species, i.e., with a low heat of adsorption, and differing from the stable, fully adsorbed species. It is also supposed to be very reactive [14].

2. Simple example

Let us start (in order to introduce our notations) with the simple text book example [1] of a unimolecular reaction, preceded by an adsorption equilibrium:

$$A + * \rightleftharpoons A' \rightarrow B \tag{2}$$

The adsorption equilibrium can be written as

$$K' = [A']/[A][*]. \tag{3}$$

According to the assumptions, the rate is

$$\text{rate} = d[B]/dt = k'[A'], \tag{4}$$

where the format of the coefficients is chosen so that it agrees with the units chosen for the concentrations of A and A′ respectively. * is representing a free adsorption site. Combining the expressions we have

$$\text{rate} = k'K'[A][*]. \tag{5}$$

Then, under the assumption that

$$1 = [A'] + [*], \tag{6}$$

$$[*] = (1 + K'[A])^{-1}, \tag{7}$$

we get

$$\text{rate} = k'K'[A](1 + K'[A])^{-1}. \tag{8}$$

Under conditions such that $1 \gg K'[A]$, the rate is proportional to [A]. Hence the formal rate constant,

$$k_{\text{exp}} = k'K', \tag{9}$$

$$\ln K' = \ln K'_0 + Q'_a/RT, \tag{10}$$

$$\ln k' = \ln k'_0 - E'/RT, \tag{11}$$

$$d(\ln \text{rate})/d(1/T) = -E_{\text{exp}}/R, \tag{12}$$

$$E_{\text{exp}} = E' - Q'_a. \tag{13}$$

3. The transient species as rate determining

Suppose now that we face a more complex situation, in the sense that it is *not* the strongly adsorbed species A′ that carries the reaction. Let us rather suppose that conditions are such that another species, a "transient" that we call A″, is the prevailing reacting species. For simplicity we assume that the two adsorbed species are in equilibrium:

$$A' \rightleftharpoons A + * \rightleftharpoons A'' \rightarrow B \tag{14}$$

Analogously to the above we write

$$K'' = [A'']/[A][*], \tag{15}$$

$$\text{rate} = d[B]/dt = k''[A''] = k''K''[A][*], \tag{16}$$

$$1 = [A'] + [A''] + [*]. \tag{17}$$

Under conditions such that the transient concentration is small compared to $[A'] + [*]$ we have

$$\text{rate} = k''K''[A](1 + K'[A])^{-1}. \tag{18}$$

Now introducing the expressions

$$\ln k'' = \ln k''_0 - E''/RT, \tag{19}$$

$$\ln K'' = \ln K''_0 + Q''_a/RT, \tag{20}$$

we get

$$\begin{aligned} d(\ln \text{rate})/d(1/T) &= -E''/R + Q''_a/R - [A](1 + K'[A])^{-1}\, dK'/d(1/T) \\ &= -E''/R + Q''_a/R - K'[A](Q'_a/R)(1 + K'[A])^{-1}. \end{aligned} \tag{21}$$

In analogy to eq. (13) we obtain

$$E_{\text{exp}} = E'' - (Q''_a - K'[A]Q'_a(1 + K'[A])^{-1}). \tag{22}$$

Consequently, if [A] approaches zero

$$E_{\text{exp}} = E'' - Q''_a \tag{23}$$

and as Q''_a *is assumed to be small* compared to "ordinary" chemical heats of reaction there is a negligible difference between E_{exp} and E (i.e. E'' in the present case). Even more, the small value of Q''_a that might be, is counteracted by the term $K'[A]Q'_a$ (eq. (22)). $K'[A]Q'_a$ is only a small fraction of Q'_a at conditions where $1 \gg K'[A]$ and consequently comparable in size with Q''_a.

4. Conclusions

One notes that the condition required to explain the observed stepwise change of activation energies and the isokinetic effect is fulfilled if the "transient" is the reacting species.

Moreover, the kinetics, in the sense of the dependence of the rate on reactant concentrations, is still governed by the adsorption equilibria that relate to the strongly adsorbed species, eq. (18). Hence it is permitted to construct reaction sequences that contain information on the reactive species from an analysis of the isokinetic effect at the same time as one might use data from, e.g., adsorption isotherms. The sum in parentheses in eq. (22) can be positive as well as negative, of possible importance to explain some observations of positive adsorption enthalpies from kinetic analysis [15].

One might ask why $k''_0 > k'_0$, a necessary condition for rate″ > rate′. Probably the loosely bound complex has less chance of loosing acquired energy by interaction with the solid phase than the strongly adsorbed species has. Hence the energy of activation is more efficiently used, a fact that will increase the preexponential factor.

One might further ask, why the transient species is able to react, when it is not forming a full chemical bond with the substrate. In the present context the original problem is formulated within the concept of selective energy transfer [10] and the question should be answered in the terms of this model. As long as the reactive vibration [10] of the transient is activated in a proper way from the heat bath vibrations, this species should be as reactive as any one more firmly bonded molecule. Thus there is no inconsistency in the model.

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