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Letter

Eyring transition-state theory and kinetics in catalysis

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Abstract

It is shown that for catalysis in general the kinetics of reactions can be discussed in terms of an extended Eyring rate equation which takes account of equilibria between free reactants and catalyst–reactant complexes as well as the equilibrium between complexed reactants and transition state. This extended equation, $k_{exp} = kT/h \cdot K_{ads} \cdot K^{\neq}$, where K_{ads} incorporates all the complexation or Langmuir adsorption coefficients necessary is the basis of a novel understanding of the well-known compensation effect.

Keywords: Compensation effect; Eyring transition-state theory; Kinetics

It is usually assumed that the equilibrium constant, $K^{\neq}$, in the famous Eyring rate equation, Eq. 1, is for one step, the chemical transformation of reactant(s) into the transition state; k_{exp} is the rate constant for the reaction.

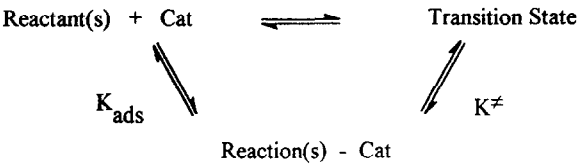
$$k_{exp} = kT/h \cdot K^{\neq} \quad (1)$$

However, we recently realized [1] that it is more valid generally to regard this equilibrium constant as applying to physical equilibrium between reactant(s) and transition state. Now a whole series of steps may be incorporated, such that $K^{\neq}$ becomes a composite constant, i.e, a multiple and/or quotient of all the individual equilibrium constants, one for each step.

This idea is particularly apposite for catalysis, homogeneous and heterogeneous, where various complexation or chemisorption steps occur prior to the activation step.

The Eyring equation is then expanded, as in Eq. 2

$$k_{exp} = kT/h \cdot K_{ads} \cdot K^{\neq} \quad (2)$$



This equation reveals that in catalysis the apparent activation energies are greatly influenced by heats of adsorption or complexation of reactant(s), while the corresponding entropies of binding the substrates to the catalyst are a major factor in determining the magnitude of the experimental pre-exponential factor, A, in the Arrhenius rate equation (3).

$$k_{exp} = Ae^{-E/RT} \quad (3)$$

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K_{ads} for heterogeneous catalysis is a Langmuir adsorption coefficient, or multiple, or quotient of such coefficients, if there is more than one reactant. This novel combination of Langmuir theory and Eyring rate theory affords the following three classical limiting cases, where C_X and C_Y are Langmuir adsorption coefficients.

$$k_{exp} = kT/h \cdot C_{X \cdot K^{\neq}} \quad (4)$$

$$k_{exp} = kT/h \cdot C_X C_Y \cdot K^{\neq} \quad (5)$$

$$k_{exp} = kT/h \cdot C_X / C_Y \cdot K^{\neq} \quad (6)$$

Eqs. 4 and 5 are for weak adsorption of reactant, or of both reactants X and Y. The heats of adsorption then subtract from the true activation energy, thereby giving a lower apparent activation energy for the overall catalytic reaction. The entropy of adsorption is also negative so A decreases as E_{app} decreases in accordance with the following Eqs/ 7, 8 and 9.

$$A = kT/h \cdot e^{\Delta S/R} \quad (7)$$

$$\Delta S = \Delta S^0_{ads(X)} + \Delta S^{\neq} \quad (8)$$

$$\Delta S = \Delta S^0_{ads(X)} + \Delta S^0_{ads(Y)} + \Delta S^{\neq} \quad (9)$$

The apparent activation energy is then given by Eqs. 10 and 11 when e and f are small constants

$$E_{app} = \Delta H^0_{ads(X)} + \Delta H^{\neq} + e \quad (10)$$

$$E_{app} = \Delta H^0_{ads(X)} + \Delta H^0_{ads(Y)} + \Delta Hf \quad (11)$$

We have argued [1] that this is the source of the famous compensation effect in catalysis [2], which is expressed by the linear relationship (Eq. 12), where a and b are constants.

$$\ln A = aE + b \quad (12)$$

Compensation may extend over a range of E values differing by as much as 200 kJ mol^{-1}, as observed recently [3].

Eq. 6 applies in those important cases where X and Y compete for the same sites, X being weakly adsorbed, and Y strongly adsorbed. Now the overall ΔS value is given by Eq. 13,

$$\Delta S = \Delta S^0_{ads(X)} - \Delta S^0_{ads(Y)} + \Delta S^{\neq} \quad (13)$$

while E_{app} is given by Eq. 14, where g is a constant

$$E_{app} = \Delta H^0_{ads(X)} - \Delta H^0_{ads(Y)} + \Delta H^{\neq} + g \quad (14)$$

It is obvious that E_{app} may rise to very high values because $-\Delta H^0_{ads(Y)}$ for the strongly adsorbing Y is now a major positive contribution. This is presumably the explanation of the very high E values at the upper end of the compensation range observed for neopentane hydrogenolysis on various Pd-zeolite catalysts [3]. Here Y is H_2 which dissociatively chemisorbs more readily than neopentane on the metal. The pre-exponential factor also increases because $-\Delta S^0_{ads(Y)}$ is now a large positive contribution to the overall value of ΔS, as given by Eq. 13.

The general value of this novel approach to kinetics in catalysis is well illustrated by a reappraisal of an important classical example from the gas phase. The halogen gases, Cl_2, Br_2, and I_2 catalyse the thermal decomposition of N_2O into N_2 and O_2 [4]. The rate of reaction is given by the expression, $k_{exp}\, P^{1/2}_{X_2} P_{N_2O}$ where X_2 is halogen and X atoms act as the catalyst. These kinetics can be explained by Scheme 1.

$$N_2O + X_2 \rightleftharpoons N_2 + \tfrac{1}{2}O_2 + X_2$$

$$X_2 \rightleftharpoons 2X \qquad K \text{ (equilibrium)}$$

$$\left.\begin{array}{l} N_2O + X \rightarrow N_2OX^{*} \\ N_2OX^{*} \rightarrow N_2 + OX \end{array}\right\} k_1 \text{(slow)}$$

$$2OX \rightarrow O_2 + X_2$$

$$k_{exp} = kT/h \cdot K^{1/2} \cdot K^{*} = k_1 \cdot k^{1/2}$$

$$E_{exp} = E_1 + \tfrac{1}{2}\Delta H^0 = E_1 + \tfrac{1}{2}[D_{X_2} + RT]$$

$$\Delta S = \tfrac{1}{2}\Delta S^0_{(X_2 \rightarrow 2X)} + \Delta S^{*}$$

Scheme 1.

A composite equilibrium, $X_2 + 2N_2O \rightleftharpoons 2N_2OX^{*}$, incorporating the formation of the catalyst X from X_2, and the complexation step between reactant and catalyst, which is also the activation step, is also involved here, and an extended Eyring equation, exactly analogous to Eq. 2 is required. The heat of dissociation of X_2 is

positive and thus E_{exp} is raised above E_1, while the entropy of dissociation of X_2, which is also positive, increases the value of the pre-exponential factor.

The extended Eyring equation, as shown by Eq. 2 and Scheme 1, therefore seems to be required to explain kinetics in catalysis for all phases, gas, liquid, and solid.

An analogous extended Eyring equation (Eq. 15) can also be used to explain isokinetic behaviour when a family of solvents is examined for their influence on the rates of a given reaction [5].

$$k_{exp} = kT/h \cdot K_{solv} \cdot K^{\neq} \quad (15)$$

Here K_{solv} is a constant arising from a constant free energy difference between solvation of reactants and transition state. The enthalpies and entropies of solvation are then important interdependent valuables ($\Delta H_{solv} - T\Delta S_{solv} = \Delta G_{solv} \simeq$ constant), just as they are for complexation and chemisorption of the reactants in catalysis [1].

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