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DISSOCIATIVE CHEMISORPTION AND SURFACE RESTRUCTURING: A SIMPLISTIC MODEL

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The cooperative mechanism for dissociative chemisorption is discussed using a very simple, ‘all or none’ model. This suffices to recover the essential aspects of the equilibrium behavior. In particular it is pointed out that the mechanism is equally applicable either to molecules which dissociate already at very low temperatures or those at which low temperatures are physisorbed. A similar mechanism can operate for interconversion of two adsorbed species. The physical assumptions of the model are discussed.

Keywords: Simple model of surface restructuring, dissociative chemisorption model

1. Introduction

Dissociative chemisorption is but one example where a strong chemical bond is broken when a molecule is adsorbed. In the gas phase such a process is very endothermic. Significant dissociation occurs only at elevated temperatures and there is a wide temperature range over which both the molecule and its dissociation products coexist in equilibrium. From a thermodynamic point of view the dissociation process in the gas phase is driven by the large increase in entropy which accrues when instead of a bound AB molecule we have two unbound fragments; The largest contribution to the change in entropy being the translational term.

At the surface, the energy required for bond breaking is provided by the formation of new bonds to the surface atoms [1,2]. Equally, the entropic considerations can be quite different from those in the gas phase. Unless a product desorbs (as in recombinative desorption) the change in entropy per a single molecule undergoing reaction on a surface is unlikely to be large. Yet the temperature dependence of bond breaking/forming processes on surfaces [3] cannot always be easily accounted for. In particular we have in mind the rather narrow temperature range over which the interconversion of species is found to occur on the surface for a variety of dissociation processes (e.g., [3,4]). This, in contrast to the situation in the gas phase.

When a product desorbs into a low pressure gas phase the system is de facto not in equilibrium. Results of thermally programmed desorption experiments are typically plotted as coverage vs. temperature. Such plots often exhibit a rapid temperature dependence of the coverage. This can be due to the removal of the product by desorption, and is not what this paper is about. To completely avoid this issue we assume that both reactant(s) and product(s) remain absorbed. Elsewhere, using a kinetic point of view, we intend to remove this restriction.

What we consider is the reaction $AB \rightleftarrows A + B$ for species adsorbed on the surface. Our purpose is to argue that due to the need of A and B to be chemically bound to the surface, such a reaction can exhibit an unusual temperature dependence; That over a narrow temperature interval the coverage can change from being primarily AB to primarily A and B, *or* vice versa. It needs emphasis that the mechanism allows either AB or A and B to be the predominant constituent at the lower temperature. The prediction of the mechanism is that at most temperatures there is but one dominant type of coverage, i.e. at any T most AB molecules either have or have not dissociated. It depends on both energetic and entropic factors whether AB is dissociated mainly below or mainly above the transition temperature.

2. The assumptions

The cooperative mechanism is based on two physically motivated assumptions. These assumptions are intuitively reasonable. The experimental evidence in support of these assumptions, as reviewed in our earlier papers [5,6], is as yet incomplete. What we therefore describe is a possible mechanism that awaits further experimental checks.

At lower temperatures, the energy required to break the A-B bond is provided by chemical-strength interaction between the dissociation products (A and B) and the surface. At the site where A-B dissociated there must be a local redistribution of electronic charge. Such a redistribution is usually accompanied by a shift in interatomic distances. This local distortion causes a strain on the surface if the adjacent surface sites are bare. This assumption will ultimately be checked by quantum chemical computations. As an interim measure we note an implication: the dissociation probability of a single molecule on an otherwise clean, bare, surface will be low at low temperatures.

If there are several molecules on adjacent sites on the surface and they all dissociate, then much of the strain can be relieved by a restructuring of the surface.

Elsewhere [5], we have shown that our assumptions will lead to a cooperative behavior. We emphasize that the reason is not an interaction between the adsorbed molecule. Rather, it is that it is energetically advantageous for a molecule to dissociate if its near neighbors also dissociate, and so on.

In this paper we simplify the theory by making an 'all or none' approximation [7]. We only allow the N molecules in a region on the surface to be either *all* dissociated or not. This avoids the mathematics required for the more realistic case [5] where there are islands of different numbers of molecules. We emphasize that the formation of these islands is a prediction of the full model. The driving force for formation of the islands being the need to relieve the local strain upon dissociation. Here, we simply stipulate the existence of many independent islands of identical size N and ask: are the molecules therein dissociated or not.

3. The all or none model

On the basis of our physical considerations we assume that a group of neighbouring N AB molecules on the surface can be only in one of two forms: All N molecules have dissociated or none has. This assumption is not made in the more detailed model [5,6]. It is introduced here since it offers a rather simple derivation of the main conclusion of our proposed equilibrium mechanism [5]. An equivalent kinetic model will be discussed elsewhere.

We imagine many 'islands' of N molecules each, on the surface. The islands are physically disjoint and so are independent. We emphasize that in a real system there will be a distribution in the size of the islands since we are *not* invoking any lateral interactions amongst the AB molecules.

Let Q_{AB} be the partition function for an undissociated AB molecule on the surface. $Q_{\mathrm{A}} Q_{\mathrm{B}}$ is the partition function for the two dissociation products. In the all or none model any molecule that did dissociate has neighbors that are also dissociated. Hence the equilibrium constant s

$$s = Q_{\mathrm{A}} Q_{\mathrm{B}} / Q_{\mathrm{AB}} \tag{1}$$

does not include the surface strain contribution to the free energy of dissociation,

$$\ln s = (\Delta S/R) - \Delta E/RT. \tag{2}$$

Here, ΔS and ΔE are the changes in entropy and energy upon dissociation

$$\Delta S = S_{\mathrm{AB}} - (S_{\mathrm{A}} + S_{\mathrm{B}}) \tag{3}$$

$$-\Delta E = E_{\mathrm{AB}} - (E_{\mathrm{A}} + E_{\mathrm{B}}). \tag{4}$$

As always, $\ln s$ is an increasing or decreasing function of $1/T$ depending on the sign of ΔE. Hence, as T is increased one can have either the dissociation *or* the recombination be favored, depending on the sign of ΔE for the specific case under consideration. Either way, we are talking of a process that *can* take place so that, as T varies, the equilibrium constant $s(T)$ must change from below unity to above unity. If over the temperature range of interest $s(T)$ is invariably well above unity (or, invariably below), no noticeable chemical change will take place. It follows that in eq. (2), the sign of ΔS and of ΔE must be the same so that there is a temperature T_s, the transition temperature, such that $\ln s(T_s) = 0$.

The molecules on the surface are taken here to be localized. The partition function (= the thermodynamic probability) of an island of N undissociated molecules is Q_{AB}^N. The partition function for an island of N dissociated molecules is $Q_A^N Q_B^N$. The partition function for an island of N molecules is

$$\begin{aligned} Q &= Q_{AB}^N + Q_A^N Q_B^N \\ &= Q_{AB}^N(1+s^N). \end{aligned} \tag{5}$$

All equilibrium properties of the system can now be computed from its partition function. Of prime interest is the fraction α of molecules that are dissociated. Each island where a dissociation occurred contributes N to the number of dissociated molecules. Hence

$$\begin{aligned} \alpha &= N(Q_A Q_B)^N/NQ \\ &= s^N/(1+s^N). \end{aligned} \tag{6}$$

It is this ease of computing α that recommends the 'all or none model'. If N is variable, as in [5,6], the computation is technically far more demanding.

The point of the proposed mechanism is the comparison of the result (6) with that when each molecule can act independently, $(N=1)$

$$\alpha = s/(1+s), \quad N=1. \tag{7}$$

This result is the same as for dissociation of AB in the gas phase. The role of the surface is then to modify the values of the changes in energy and entropy upon dissociation. Such changes can be quite dramatic and can lead to a very significant reduction in the value of the transition temperature T_s, $s(T_s) = 1$. For

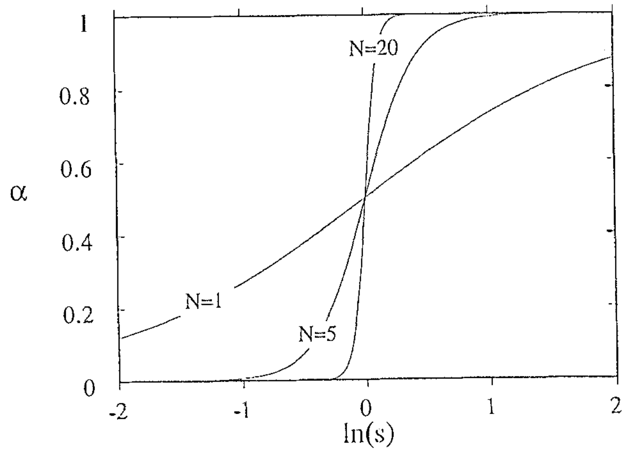

Fig. 1. The mean fraction α of adsorbed molecules which have dissociated vs. ln s, cf. eq. (6). Note that $\ln s$ is linear in $1/T$ with the slope $-\Delta E$, cf. eq. (2), which can be of either sign. At the transition temperature T_s, $\ln s = 0$. N is the (here, fixed) number of molecules which dissociate in a cooperative fashion. $N=1$ is the case where every molecule acts independently. The results are shown for $N=1$, 5, 20. As $N \to \infty$, α changes abruptly at T_s from zero to unity.

$N = 1$, the dependence of α on s is however the same in the gas phase and on the surface for $N = 1$: As s increases from below unity to above it, α gradually changes from below 0.5 to above it.

When dissociation requires the cooperation of several molecules ($N > 1$), then for most values of s, the fraction of molecules which have dissociated is either well below 0.5 or well above it. The reason is that, for $N > 1$, if $s < 1$, then $s^N \ll 1$ and $\alpha \ll 0.5$. If $s > 1$, then $s^N \gg 1$ and $\alpha \gg 0.5$. Only near the transition temperature when $s \approx 1$, can α be near to 0.5. As T, and hence s, change there is a fairly abrupt switch from mostly one type of coverage to another, fig. 1. The higher the value of the island size N, the more abrupt is the change.

The transition from quite low to a near unity value for the coverage α occurs as s increases, and passes through the value of unity. We mention the point made earlier that s varies (roughly) linearly with $1/T$ with a slope whose sign is opposite to that of ΔE. As T is increased one can have s either increases or decrease, depending on the system at hand. It is not necessarily the case that the switch is from mostly AB to mostly A and B as the temperature is increased. The opposite is also possible. The signature of the cooperative behavior is the narrow range in temperature over which the change in the nature of the coverage of the surface occurs. Equally, unless $s(T)$ can cross the value of unity, the nature of the coverage will remain largely unchanged with temperature (provided of course that other processes which are not allowed for in the model do not occur).

4. The transition temperature

The temperature T_s at which the conversion from predominantly one type of coverage to the other occurs is, cf. (2),

$$T_s \Delta S = \Delta E. \tag{8}$$

Here, ΔE is the change in energy upon bond breaking and similarly for ΔS. This result is valid provided the system is and remains in equilibrium and holds also in the more elaborate models for the proposed mechanism.

If the bond breaking is $AB \rightarrow A + B$ and the surface process is exothermic, $\Delta E < 0$, so that the products are more tightly bound to the substrate, we require $\Delta S < 0$. Chemically this is reasonable. The physisorbed undissociated AB molecule is less constrained than the chemisorbed fragments. If the surface process is endothermic we require $\Delta S > 0$. Note that processes of the type AB(ad) → A(ad) + B(gas) or at least when B is mobile on the surface, fall into this category.

The value of ΔE is determined primarily by the strength of binding of the products to the surface,

$$\Delta E = \Delta E(\text{gas phase}) + (E((\text{A}) + E(\text{B})) - E(\text{AB})). \tag{9}$$

Here, $E(X)$ is the binding energy of X to the surface with the zero of energy being for an unbound species in the gas phase. In general, ΔE (gas phase) is positive (and large). The tigther is the surface bond to the products, the lower is ΔE. Rough or more open surface faces will exhibit a lower transition temperature. What cannot be provided by an equilibrium model is why rough surfaces can also exhibit a high turnover rate, [6,8].

5. The work of desorption

The thermodynamic measure of the work required to remove a molecule is the chemical potential, μ,

$$-\mu/RT = (\partial \ln Q/\partial N)_T = \ln Q_{AB} + \frac{s^N}{1+s^N} \ln s \tag{10}$$

Using (6) for α

$$-\mu/RT = \ln Q_{AB} + \alpha \ln s = (1-\alpha) \ln Q_{AB} + \alpha \ln(Q_A Q_B). \tag{11}$$

Hence, if we keep α fixed, the work required is just what one would intuitively expect. Say, however, we change the temperature sufficiently slowly that at any T the reaction adjusts to its equilibrium value at that temperature. If the interval over which T is changed includes T_s, α would change rapidly over the interval and so would the work required to desorb a molecule. Note that the work of desorption is invariably lower at the higher temperature.

The fraction α in the model is the fraction of all molecules on the surface which are dissociated. It is not the same as the coverage. In the simple model presented here, the number N of molecules per island is fixed. There are reports in the literature regarding the dependence of the activation energy for desorption on the coverage. Note that in our mechanism there are no lateral interactions between adsorbed molecules: No direct interactions nor surface-mediated interactions which result from surface reconstruction induced by adsorption. The restructuring of the surface we are concerned with here is due to the charge redistribution which accompanies chemical bond breaking/forming in the already adsorbed molecules.

6. Concluding remarks

A simple model which exhibits bond breaking (or forming) occurring preferentially over a narrow temperature range has been discussed. To achieve a simple model the chemical physics of the problem has been reduced to a caricature of the actual situation. Yet, the essential result is the same as in more elaborate models. The physical assumption of the mechanism is the implication of reorganisation of electronic structure of the system upon dissociation. We assume it to be accompanied by a distortion of the substrate; a distortion which can be alleviated when many adjacent molecules dissociate. We reiterate that this adsorbate-induced restructuring of the clean, bare, substrate is concomitant with bond breaking (and not with mere adsorption). It remains to be seen whether such an effect can be important for systems which are not in equilibrium.

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