

**EFFECTS OF ADSORBATE ISLANDING
ON REACTION KINETICS AND THERMAL DESORPTION SPECTRA:
A MONTE CARLO-QUASICHEMICAL MODEL**

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The role of adsorbate lateral interactions in surface reaction kinetics is studied for bimolecular reactions $A + B \rightarrow AB$. One reactant (A) tends to aggregate into islands, B is mobile and AB is a rapidly desorbing product. A model combining Monte Carlo dynamics for the slow processes (A-aggregation and AB-formation) and an appropriately modified quasichemical approximation for the fast ones (B-redistribution) is used to calculate reaction rates. Reaction desorption spectra and activation energies are calculated for different initial conditions and adsorbate lateral interactions.

1. Introduction

Interest in the effects of adsorbate lateral interactions and aggregation (islanding) on surface kinetic processes in chemisorbed systems is growing rapidly. Finite metastable adsorbate islands are formed when lateral interactions are strong enough to favor formation of ordered overlayers, but the experimental time scale is too short for complete phase separation [1]. Monte Carlo (MC) simulations reveal that the long-lived islands often exhibit indented boundaries and non-simple area-perimeter ratios [2,3]. If another reactant is co-adsorbed between (and possibly within) the islands, complicated kinetic behavior is expected depending on initial conditions, interaction parameters, diffusion and reaction rates. A well-known system exhibiting such complex behavior is $O(a) + CO(a) \rightarrow CO_2(g)$ (a =adsorbed, g =gas) on metal surfaces [4,5].

Information on reaction kinetics is readily obtained from temperature programmed reaction spectroscopy (TPRS) provided the reactant distribution is random [6]. Complications due to lateral interactions have been examined using equilibrium lattice gas models [7,8]. However these are inadequate if adspecies are aggregated in (non-equilibrium) islands. Alternatively, rate equations have been

derived assuming highly idealized island patterns [9]. Rate equations have also been proposed to account for lateral interactions and different mobilities of the adsorbed reagents but without explicitly accounting for phase separation and islanding [10]. Several recent MC studies have examined the role of islanding in chemisorbed systems. Hood et al. [11] have demonstrated the effects of aggregation on thermal desorption spectra in a system containing a single species ($2N \rightarrow N_2$ on Ru(001); a related problem is dealt with in ref. [12]). Other MC models deal with aggregation due to selective reaction in steady state systems, in which the adsorbates do not diffuse on the surface [13].

We have previously studied the effects of island formation by one adsorbate (during a disorder-order phase transition) on the kinetics of bimolecular surface reactions using MC dynamics for all kinetic processes, for constant temperature [3]. Extending this procedure to varying temperature conditions, such as in TPRS experiments, and for arbitrary lateral interactions w_{ij} ($i, j=A, B$) often implies prohibitively long computational times. One of our major objectives in this Letter is to demonstrate that in most cases of interest the modeling procedure can be greatly simplified by applying the ("expensive") MC dynamics only for the slow proc-

esses (A-aggregation and AB-formation). On the other hand, the fast ones, in our case the redistribution of the highly mobile species B among the A-islands, can be accounted for by appropriately modified equilibrium lattice gas models, e.g. the quasi-chemical approximation (QCA). In this Letter we briefly describe our combined MC QCA approach and apply it to calculate thermal desorption spectra for different initial conditions and various lateral interaction parameters w_{ij} . We also comment on the derivation of the modified QCA (to be published in more detail elsewhere).

2. Kinetic model

Consider a bimolecular reaction $A(a) + B(a) \rightarrow AB(g)$ in which one reactant, A, shows a strong aggregation tendency and slow diffusion, the other, B, is relatively mobile, and AB is a rapidly desorbing product. Explicitly, we assume that for temperatures where reaction occurs $\tau_B \ll \tau_R, \tau_A$ where τ_A (τ_B) is the diffusion time (reciprocal jump frequency) of A (B) and τ_R is the reaction time of an AB-pair. The system is modeled as a lattice gas mixture with nearest neighbor (nn) lateral interactions w_{ij} , ($ij=AA, BB, AB$). The applicability of our approach is intimately related to the hierarchy of time scales, $\tau_B \ll \tau_R, \tau_A$: Because of the fast diffusion of B-atoms their distribution on the surface, $\{B\}$, is *instantaneously equilibrated* following any change in the configuration of A-atoms, $\{A\}$, due to reaction, migration or desorption. We calculate $\{B\}$ by a modified version of the quasi-chemical approximation (QCA) [14]. On the other hand, the slow processes – A-diffusion (and aggregation) and AB-formation–desorption – which modify the (non-equilibrium) $\{A\}$ are modeled by MC dynamics. All simulations have been performed on a 500×500 square lattice with periodic boundary conditions. The present “MC QCA” approach saves MC modeling of B-diffusion, which for $\tau_R \gg \tau_B$ requires many MC steps per reactive event and is therefore computationally expensive, especially for arbitrary w_{ij} and changing T .

Our reaction scheme consists of two distinct stages: (i) A-adsorption and aggregation ($0 \leq t \leq t_D$); (ii) B-adsorption, diffusion and reaction with A ($t \geq t_D$). In

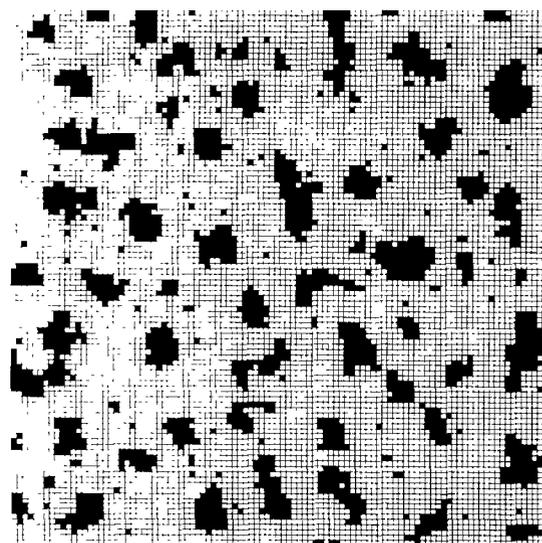


Fig. 1. A 100×100 slab of the 500×500 lattice showing typical island pattern after 500 MCS, $w_{AA}/kT_A = -2.5$, $\theta_A = 0.2$. Larger but similarly ramified islands for higher θ are shown e.g. in ref. [3].

more detail: (i) At $t=0$ A-atoms are adsorbed with initial coverage θ_A^0 on a surface at temperature T_A . The initial $\{A\}$ is assumed random. Subsequent hopping of As between adjacent lattice sites is modeled by conserved (Kawasaki) MC dynamics (see e.g. refs. [2,3]). We assume attractive AA-interactions, $w_{AA} = -2$ kcal/mole, which corresponds to a critical lattice gas temperature $T_c \approx 570$ K [14]. Thus for all T_A well below T_c the A-atoms tend to irreversibly aggregate in 1×1 ordered domains. ($T_A = 400$ K in the simulations.) Aggregation times are conveniently measured in MC steps (MCS) corresponding to one attempted jump per particle [2,3]. After ≈ 1000 MCS most As are aggregated and further island growth slows down drastically. The islands characterizing this long-lived stage appear as in fig. 1. (ii) At $t=t_D$ we reset $T=T_0$, adsorb B and start a linear temperature sweep: $T(t) = T_0 + \beta(t - t_D)$. We typically use $T_0 = 250$ K (at which reaction is negligible) and $\beta = 10$ K/s. A-migration during the reaction period is neglected (i.e. $\tau_A \gg \tau_R \gg \tau_B$). Similarly we ignore non-reactive desorption of A and B. Reaction can only occur between A and B on nn-sites.

The reaction rate $R = -d\theta_A/dt = -\beta d\theta_A/dT$ is calculated as follows. Given the instantaneous values $\{A\}$, θ_B , and T , we use the modified QCA – see

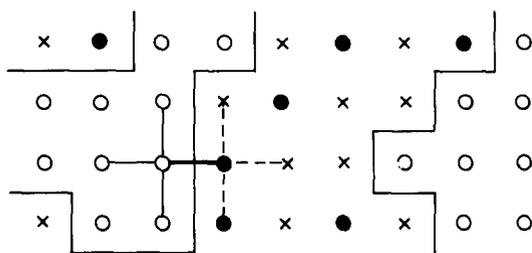


Fig. 2. An example demonstrating the calculation of $q(A_m, T)$ using the modified QCLA. \circ = A-atoms (in islands), \bullet = B-atoms, \times = vacant sites. The potentially reactive $(A_m, B_n)_s$ pair is designated by a heavy solid line. Three AA-, one AB- and two B0-bonds determine s . In this case $P(B_n, s|A_m) \approx P_e(A, B) P_b(B, B) P_b(B, 0)$ and $E_s = 3w_{AA} + w_{BB}$, see text.

below - to compute $P(B_n, s|A_m)$, the conditional probability that if site m is occupied by A, a nn-site n will be occupied by B and the "neighborhood" of the pair is s . $s \equiv k, l, k', l'$ (≤ 3) where k, l (k', l') are, respectively, the numbers of A- and B-neighbors of A_m (B_n), see fig. 2. We use $q_0(T) = \nu_R \exp(-E_0/kT)$ for the reaction probability per unit time of an isolated AB-pair. The corresponding probability for an $(A_m, B_n)_s$ pair is taken as $q_s(T) = q_0(T) \exp(\gamma E_s/kT)$, where $E_s = kw_{AA} + (l+k')w_{AB} + l'w_{BB}$ is the interaction energy of the pair with its neighbors. γ is a coupling parameter measuring the excess activation energy due to lateral interactions, which may be related to the properties ("tightness") of the transition state of the reactive AB-pair [8]. In the results below we use $\gamma = 1$ or $\gamma = 0$ and $E_0 = 24$ kcal/mole. ν_R , typically $\approx 10^{15} \text{ s}^{-1}$, only sets the reaction time scale.

The reaction probability per unit time of A_m is

$$q(A_m, T) = \nu_R \sum_{n,s} P(B_n, s|A_m) \exp[-(E_0 - \gamma E_s)/kT] \quad (1)$$

and the total rate (per site) is

$$R = -\beta \dot{\theta}_A = M^{-1} \sum_m \delta(m, A) q(A_m, T), \quad (2)$$

where $\delta(m, A) = 1$ if site m is occupied by A and 0 otherwise, and M is the lattice size. Note that $\sum_s P(B_n, s|A_m) = P(B_n|A_m)$ is the probability of site n being occupied by B. Because of lateral interactions $P(B_n|A_m)$, hence R , depend on $\{A\}$, w_{ij} , T , and θ_B ,

even if $\gamma = 0$. This dependence accounts for local concentration effects which may affect R even in the absence of the (direct) "energetic effect" associated with E_s (e.g. if $\gamma = 0$). It is easily verified that when all $w_{ij} = 0$ (random A, B) we obtain $R = zq_0(T) \theta_A \theta_B$, where z is the lattice coordination number. The MC procedure for calculating R is simple: T is increased in small intervals ΔT (≤ 1 K) such that $r(m, T) = [q(A_m, T)/q_0(T)] \Delta T \ll 1$ for all A_m . Each A_m reacts with B (and desorbs as AB) with probability $r(m, T)$ and the rate is calculated by (2). At the end of the ΔT interval the new $\{A\}$ is recorded, $T \rightarrow T + \Delta T$, $\theta_B \rightarrow \theta_B - \Delta\theta_B$ with $\Delta\theta_B = \Delta\theta_A$, $P(B_n, s|A_k)$ is calculated for the new $\{A\}$, θ and T , etc.

3. The modified quasichemical approximation

The QCA is often used to calculate thermodynamic properties and/or (lattice) distribution functions for *equilibrium* systems [14]. It may be derived starting with the assumption that the probability $P(i_1, \dots, i_M)$ of a given lattice configuration is proportional to the product of pair ("bond") probabilities $P(i_k, i_l)$ over all lattice bonds [3]. For an A, B mixture $i_k = A, B, 0$ ($0 = \text{vacancy}$). The $P(i, j)$ are determined by minimizing the free energy functional $F = \sum_{ij} P(i, j) [w_{ij} + kT \ln P(i, j)]$ subject to particle conservation constraints. This yields the $P(i, j)$ which can be used to compute R for $A + B \rightarrow AB$ [3,7,8], provided *both* A and B are *equilibrated* throughout the reaction (i.e. if $\tau_A, \tau_B \ll \tau_R$). In our *modified* QCA the instantaneous $\{A\}$ and the pattern of AA-bonds is imposed as a boundary condition, and the QCA is applied only to $\{B\}$, i.e. the distribution of B among the sites not occupied by A. Probabilities are assigned to the remaining ("non AA") nn-bonds which are classified as edge bonds whose occupation probabilities are $P_e(A, j)$ with $j = 0$ or B, and bulk bonds, with $P_b(i, j)$ and $i, j = 0$ or B. Now the average free energy per bond (not including AA-bonds) is written as $F = f_e F_e + f_b F_b$ with f_e and f_b denoting the fraction of edge and bulk bonds, respectively, and F_e and F_b the free energy associated with $P_e(A, j)$ and $P_b(i, j)$. The P_α ($\alpha = e, b$) are determined by minimizing F subject to B-atom conservation and depend on $\{A\}$ via $\{f_\alpha\}$, T , $\theta_B/(1 - \theta_A)$, w_{AB} , and w_{BB} . The $P(B_n, s|A_m)$ in (1) are (appropriately normalized) products of P_α s, fig. 2.

4. Results and discussion

Fig. 3 shows several representative TPR spectra (TPRS), i.e. R versus T curves, calculated by the MC QCA model. We use $\Omega = (w_{AA}, w_{AB}, w_{BB}; \gamma)$ with w_{ij} in kcal/mole to specify the interaction parameters and $C = (\theta_A^0, \theta_B^0; t_D)$ for the initial conditions, t_D in MCS. Fig. 3A also shows, for comparison, two spectra for limiting cases: (a) Random A, B distributions and $w_{ij} \equiv 0$ which (for $\theta_A^0 = \theta_B^0$) give $R = 4\nu_R \exp[-E_0/kT] \theta^2$. In this well-known case R is symmetrical around a peak temperature $T_p = T_p(\nu_R, E_0, \theta^0)$ [6]. For our parameters $T_p \approx 350$ K. (b) Equilibrium {A} and {B} throughout the reaction ($\tau_A, \tau_B \ll \tau_R$), calculated for $\Omega = (-2, 0, 0; 1)$, $C = (0.2, 0.2; 0)$ using the ordinary QCA for A, B mixtures [8] (see also ref. [3]). Here the likelihood for AA-pairs decreases with θ_A , hence with time. Thus the activation energy E_a - see below - is predicted to decrease monotonically to E_0 (see fig. 4). The other two TPRS in fig. 3A demonstrate the role of islanding. For $t_D = 0$ {A} is random. Here isolated As react rapidly yielding the first peak. The higher T peak is due to As initially associated in small clusters (primarily doublets at this θ_A) which react more slowly, with $E_a - E_0 - w_{AA}$, ($\gamma = 1$). Reaction turns doublets to (rapidly react-

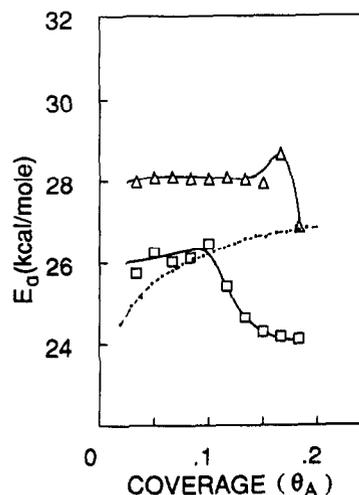


Fig. 4. Coverage dependent E_a . All curves for $\theta_A^0 = \theta_B^0 = 0.2$, $\gamma = 1$: \square $w_{AA} = -2$, $w_{AB} = w_{BB} = 0$, $t_D = 0$; \triangle as above but $t_D = 5000$; --- ordinary QCA for $w_{AA} = -2$, $w_{AB} = w_{BB} = 0$. (All w_{ij} in kcal/mole, t_D in MCS.)

ing) singlets, etc., hence the sharp termination of reaction. When $t_D = 5000$ most As are initially incorporated in islands. Those at island perimeters are

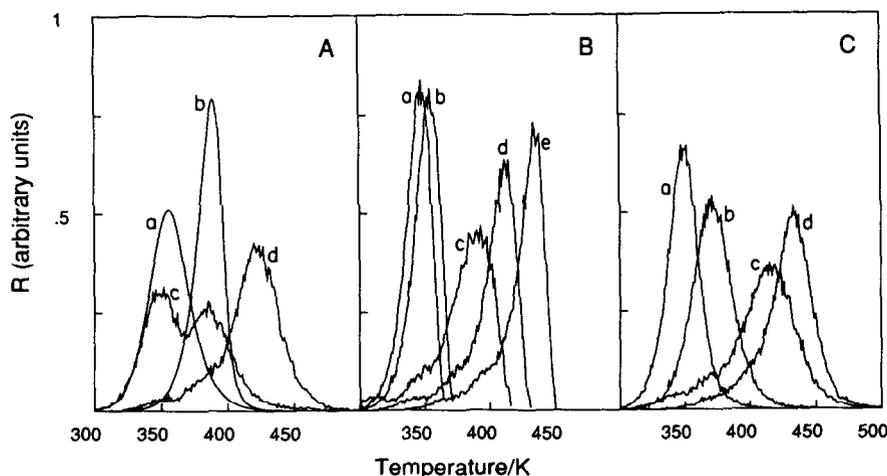


Fig. 3. Representative TPRS for $\beta = 10$ K s $^{-1}$. (A) All curves for $\theta_A^0 = \theta_B^0 = 0.2$, $w_{AB} = w_{BB} = 0$ and, except curve (a), $w_{AA} = -2$ kcal/mole and $\gamma = 1$. (a) Random A, B and $w_{ij} = 0$. (b) Ordinary QCA for A, B mixture. (c) MC QCA, $t_D = 0$ MCS. (d) MC QCA, $t_D = 5000$ MCS. All following spectra are for MC QCA $t_D = 5000$ MCS. (B) All curves for $\theta_A^0 = 0.2$, $\theta_B^0 = 0.5$, with $\Omega = (w_{AA}, w_{BB}, w_{AB}; \gamma)$ given by (a) $(-2, -1, 0; 0)$, (b) $(-2, 1, 0; 0)$, (c) $(-2, 1, 0; 1)$, (d) $(-2, 0, 0; 1)$, (e) $(-2, -1, 0; 1)$. (C) In all curves $\theta_A^0 = \theta_B^0 = 0.2$, $t_D = 5000$ MCS; Ω is (a) $(-2, 0, -1; 0)$, (b) $(-2, 0, 1; 0)$, (c) $(-2, 0, -1; 1)$, (d) $(-2, 0, 1; 1)$.

potentially reactive but, since $w_{AA} < 0$, involve higher E_a hence considerably higher T_p . As reaction proceeds the islands become smoother, smaller and fewer but E_a stays nearly constant (see fig. 4). If $\gamma = 0$ lateral interactions and islanding affect R only through local concentration effects (probably of AB-pairs). If in addition $w_{AB} = w_{BB} = 0$, $\{B\}$ is always random and w_{AA} affects R only via the island pattern at t_D . The TPRS (not shown) for $\Omega = (-2, 0, 0; 0)$ appear similar to curve (a) in fig. 3A (random A, B) for both $t_D = 0$ and 5000. This is due to the large perimeter-area ratio of the islands which for $\gamma = 0$ is enhanced as reaction proceeds [3].

All TPRS in figs. 3B and 3C are for $t_D = 5000$. Fig. 3B illustrates the role of w_{BB} . $w_{BB} < 0$ favors B segregation, thereby diminishing B-concentration near A-islands. (The opposite holds for $w_{BB} > 0$). However, the effect is small unless $\theta_B/(1 - \theta_A)$ is large. Indeed, for $\theta_B^0 = 0.2 = \theta_A^0$ the spectra corresponding to $w_{BB} = \pm 1$ are all very similar to the $w_{BB} = 0$ case (thus no spectra are shown for these cases). The effects are sizeable (fig. 3B) for larger $\theta_B^0 (= 0.5)$, but only for $\gamma = 1$. Fig. 3C displays the effects of w_{AB} . $w_{AB} > 0$ reduces B-concentration near island boundaries. Similarly $w_{AB} < 0$ enhances B-concentration near island perimeters, implying increased R for $\gamma = 0$. But for $\gamma = 1$ the increased number of bonds between reactive A- and "spectator" B-atoms also means higher reaction barriers, which offset the concentration effect (compare with curve (d) in fig. 3A).

Kinetic parameters derived from TPRS depend largely on the reaction mechanism assumed. Consider a general rate law

$$R_T = -d\theta_A/dT = (R/\beta)$$

$$= \beta^{-1} f(\theta_A, \theta_B) \exp[-E_a(\theta_A, \theta_B)/kT].$$

Note that when $w_{AB}, w_{BB} \neq 0$, E_a incorporates both barrier ($E_0 - \gamma E_s$) and concentration contributions. The latter enters via $P(B_n | A_m)$, e.g. for $w_{AB} < 0$ this probability includes an $\exp(-w_{AB}/kT)$ factor. Also, the simple exponential dependence is clearly an approximation. Further, in our problem both f_a and E_a depend on initial conditions. Yet, adopting the above R_T we can use Taylor and Weinberg's procedure [15] to derive E_a ; i.e. $E_a(\theta_A, \theta_B)$ is the slope of the $\ln R_T$ versus $1/T$ plot obtained from a series of runs with different heating rates β for the given θ_A ,

θ_B . A few E_a -curves are shown in fig. 4. The $\Omega = (-2, 0, 0; 1)$, $C = (0.2, 0.2, 5000)$ curve shows that except for a transient initial period of monomeric A-consumption, $E_a \approx \text{constant} \approx 28$ kcal/mole indicating reaction with island perimeter A-atoms, each bonded to $(E_a - E_0)/|w_{AA}| \approx 2$ other As. In contrast, for $t_D = 0$, i.e. non-aggregated A, $E_a \approx E_0$ as long as singlet As react (first peak in fig. 3A); later $E_a \approx E_0 - w_{AA} \approx 26$ kcal/mole when doublets start reacting. At variance with both cases above, the ordinary QCA predicts monotonically decreasing E_a .

5. Concluding remarks

We have demonstrated some of the effects associated with adsorbate interactions and islanding for a reactive chemisorbed system, using a newly developed modeling scheme. We have specifically referred to the effects of adsorbate aggregation on thermal desorption spectra, because they serve as a common tool for extracting kinetic information. Yet it should be noted that we do not suggest (at least not at this stage) theoretical analyses of the type presented above as a means (or an "inversion" procedure) to derive lateral interaction parameters. These may be more reliably inferred by independent measurements, e.g. from phase diagrams. Rather, our aim was mainly to demonstrate the qualitative trends, and the complications, arising from lateral interactions. The systems we have investigated are, admittedly, idealized. Nonetheless, extension to more general (and realistic) cases is, at least in principle, straightforward. For instance, by considering higher than nn interactions one can model, say, $p(2 \times 2)$, $c(2 \times 2)$ overlayers, etc. and study the effects of different lattice sites and domain boundaries (ground state degeneracies). Similarly, A-migration and A- and B-desorption can be easily included in the model. (Extension of our approach along these directions is now in progress). Of course, interaction parameters, diffusion rates and transition state characteristics are required for reliable modeling of specific systems. Such information is being steadily accumulated.

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