Dynamic Effects of Promoters on Associative Desorption

J. L. Sales,† R. O. Uñac,‡ M. V. Gargiulo,† and G. Zgrablich*,‡

Departamento de Física and IEE (CONICET), Universidad Nacional de San Juan, Av. Libertador 1100 Oeste, 5400 San Juan, Argentina and Laboratorio de Ciencias de Superficies y Medios Porosos, Universidad Nacional de San Luis, Chacabuco 917, 5700 San Luis, Argentina

Received August 16, 1999. In Final Form: December 6, 1999

The kinetics of the associative desorption of A_2 in the presence of coadsorbed promoter species B is studied under conditions of nonequilibrium by the analysis of thermal desorption spectra obtained by Monte Carlo simulation. A rich variety of behaviors is found and discussed with regard to the interplay between the concentrations of promoter species, the surface mobility of A and B, and the interparticle interactions.

Introduction

The widespread use of Monte Carlo simulation methods to analyze molecular reactions on solid surfaces in recent years has allowed the study of many processes, whose relevance ranges from pure theoretical interest to practical applications.[1−24] This success relies on the fact that from a relatively small number of microscopic mechanisms, a relatively complex reaction can be simulated to obtain insight into its behavior at the macroscopic level. In particular, these methods have been intensively applied to the study of the kinetics of heterogeneously catalyzed reactions by the analysis of thermal desorption spectra (TDS),[25] because this is the most widely used experimental technique. The kinetics of these reactions may exhibit a rich and complex dynamic behavior, which is usually not well described by the standard mean-field rate equations of chemical kinetics because these equations do not take into account such important effects as correlation among reactant species, fluctuations in their spatial distribution, their finite mobility, etc.

In the present work we focus on the study of a surface reaction that is expected to be strongly influenced by the mobility of adsorbed species. We propose the reaction:

$$A(s) + A(s) + B(s) \rightarrow A_2(g) + 2s + B(s) \qquad (1)$$

where s indicates the adsorbed phase, and/or a surface site, and g denotes the gas phase. This reaction, which corresponds to the associative desorption of species A taking place only in the presence of at least one particle of the coadsorbed species B (the promoter species), is sufficiently general to represent a variety of processes; for examples, the associative desorption of H_2 on transition metals in the presence of coadsorbed O_2[22,26] or the annihilation of particles at defect sites (in this case the species B is immobile).

Because the reaction takes place only when two A particles come in contact with a promoter B, the kinetics should be strongly dependent on the surface mobility of A and B and on their interactions. It is therefore necessary to make a dynamic study of the process under nonequilibrium conditions. The effects of surface mobility of adsorbed species on thermal desorption spectra has been investigated by Meng and Weinberg[20] in the case of monomolecular desorption. The present study is an extension of that research to a more general reaction.

In what follows, we employ a dynamic Monte Carlo method to simulate the general reaction in eq 1 and obtain TDS under different conditions of mobility and interactions of the reactants. The results are discussed and interpreted on the basis of the relevant microscopic mechanisms involved.

* Author to whom correspondence should be sent. Telephone: 54-2652-436151. Fax: 54-2652-425109. E-mail: giorgio@unsl.edu.ar.
† Departamento de Física and IEE (CONICET).
‡ Laboratorio de Ciencias de Superficies y Medios Porosos.

(1) Weinberg, W. H. *Kinetics of Interface Reactions*, Springer Series in Surface Science, Vol. 8; Grunze, M., Kreuzer, H. J., Eds.; Springer: Berlin, 1987.
(2) Hood, S. E.; Toby, B. H.; Weinberg, W. H. *Phys. Rev. Lett.* **1985**, *55*, 2437.
(3) Ziff, R. M.; Gulari, E.; Barshad, Y. *Phys. Rev. Lett.* **1986**, *56*, 2553.
(4) Ziff, R. M.; Fichthorn, K. *Phys. Rev.* **1986**, *B34*, 2038.
(5) Sales, J. L.; Zgrablich, G. *Surf. Sci.* **1987**, *187*, 1; *Phys. Rev.* **1987**, *B35*, 9520.
(6) Silverberg, M.; Ben-Shaul, A. *Chem. Phys. Lett.* **1987**, *134*, 491; *J. Chem. Phys.* **1987**, *87*, 3178; *J. Stat. Phys.* **1988**, *52*, 1179; *Surf. Sci.* **1989**, *214*, 17.
(7) Fichthorn, K.; Gulari, E.; Ziff, R. M. *Chem. Eng. Sci.* **1989**, *44*, 1403.
(8) Sales, J. L.; Zgrablich, G.; Zhdanov, V. P. *Surf. Sci.* **1989**, *209*, 208.
(9) Heras, J. M.; Velasco, P. A.; Viscido, L.; Zgrablich, G. *Langmuir* **1991**, *7*, 1124.
(10) Albano, E. V. *Phys. Rev. Lett.* **1992**, *69*, 656.
(11) Luque, J. J.; Jiménez Morales, F.; Lemos, M. C. *J. Chem. Phys.* **1992**, *96*, 8535.
(12) Ramirez Cuesta, A.; Zgrablich, G. *Surf. Sci.* **1992**, *275*, L636.
(13) Albano, E. V.; Pereyra, V. D. *J. Chem. Phys.* **1993**, *98*, 1044.
(14) Tysoe, W. T.; Ormerod, R. M.; Lambert, R. M.; Zgrablich, G.; Ramirez Cuesta, A. *J. Phys. Chem.* **1993**, *97*, 3365.
(15) Albano, E. V. *J. Phys. A. (Math., & Gen.)* **1994**, *27*, 431.
(16) Meng, B.; Weinberg, W. H.; Evans, J. W. *J. Chem. Phys.* **1994**, *101*, 3234.
(17) Zuppa, C.; Bustos, V.; Zgrablich, G. *Phys. Rev.* **1994**, *B51*, 2618.
(18) Kang, H. C.; Weinberg, W. H. *J. Chem. Phys.* **1994**, *100*, 1630.
(19) González, A. P.; Pereyra, V. D.; Milchev, A.; Zgrablich, G. *Phys. Rev. Lett.* **1995**, *75*, 3954.
(20) Meng, B.; Weinberg, W. H. *Surf. Sci.* **1997**, *374*, 443.
(21) Sales, J. L.; Uñac, R. O.; Gargiulo, M. V.; Bustos, V.; Zgrablich, G. *Langmuir* **1996**, *12*, 95.
(22) Bustos, V.; Gargiulo, M. V.; Sales, J. L.; Uñac, R. O.; Zgrablich, G. *Langmuir* **1997**, *13*, 4201.
(23) Uñac, R. O.; Sales, J. L.; Gargiulo, M. V.; Zgrablich, G. *J. Phys.: Condens. Matter* **1997**, *9*, 9469.
(24) Cortés, J.; Valencia, E. *Chem. Phys.* **1998**, *229*, 265; *Surf. Sci.* **1999**, *425*, L357.
(25) Lombardo, S. J.; Bell, A. T. *Surf. Sci. Rep.* **1991**, *13*, 1.
(26) Resch, C.; Zhukov, V.; Lugstein, A.; Berger, H. F.; Winkler, A.; Rendulic, K. D. *Chem. Phys.* **1993**, *177*, 421.

10.1021/la991099u CCC: $19.00
Published on Web 02/23/2000

Model and Simulation Method

The solid surface is represented by a regular square lattice of $M = L \times L$ sites, with periodic boundary conditions. Each site can be either empty or occupied by a single particle (*A* or *B*). The surface is initially completely covered with species *A* and *B* with coverages

$$\theta_A = N_A/M \qquad \theta_B = N_B/M = 1 - \theta_A \tag{2}$$

where N_A and N_B are the number of randomly adsorbed *A* and *B* particles, respectively. The elementary processes of diffusion jumps and reaction are considered next.

Diffusion Jumps. Any particle *X* (*A* or *B*) can migrate from an initial site *i* to an empty nearest-neighbor (NN) site through an activated jump with a probability per unit time given by

$$P^X_{di} = \nu \exp[-(E_{dX} - E^X_i)/k_B T] \tag{3}$$

where ν is a preexponential factor, E_{dx} is the activation energy for diffusion at zero coverage, and $E_i{}^x$ is the interaction energy seen by the particle at site *i*, for species *X*. If we consider only NN interaction energies (ϵ^{XY}) between a particle of species *X* and one of species *Y*, then

$$E^X{}_i = n_X \epsilon^{XX} + n_Y \epsilon^{XY} \qquad X \text{ and } Y = A \text{ or } B \tag{4}$$

where n_X (n_Y) is the number of sites NN to *i* occupied by species *X* (*Y*).

Reaction. A pair of particles of species *A*, adsorbed on a pair of NN sites (*i*,*j*), can react in the presence of species *B*, as stated by eq 1, to desorb associatively as A_2 with a probability per unit time given by

$$P_{rij} = \nu \exp[-(E_{r0} - W_{ij})/k_B T] \tag{5}$$

where E_{r0} is the activation energy barrier for reaction at zero coverage, W_{ij} is the amount by which such barrier is modified due to interactions with NN adsorbed particles, and for simplicity, we have taken the same preexponential factor as for eq 3. We assume that the activation energy barrier for reaction is very high if the pair *AA* does not have at least one NN promoter *B*, so that the reaction is only possible with the presence of a promoter. The effect of the presence of a particle of species *B* can be thought as modifying the substrate properties in such a way as to render the reaction possible with an activation energy E_{r0}. This activation energy can be further modified by lateral interactions in an amount W_{ij}. In fact, if NN interactions contribute with energy $\epsilon_r{}^{AX}$, to the reaction barrier, then

$$W_{ij} = n_A \epsilon_r^{AA} + n_B \epsilon_r^{AB} \tag{6}$$

A thermal desorption run consists of the following: once the initial distribution of particles is established at an initial temperature T_0, the temperature is increased linearly at a rate β and the number of desorbed A_2 molecules per unit temperature interval is monitored as a function of *T*. As a result, a thermal desorption spectrum is obtained. To simulate the process, we use a standard dynamic Monte Carlo method[27] with appropriate modifications for the present case.

Let P_{max} be the maximum transition probability per unit time of any elementary process in the system and *N* the total number of particles present on the surface at time *t*. The surface is prepared with the desired initial coverage of *A* and *B* species, the temperature is set to T_0, and the system is thermalized to achieve thermodynamical equilibrium for the initial state. Then the following procedure is followed:

(*i*) The temperature is increased by an amount

$$\Delta T = \beta[-\ln(\xi)/(NP_{max})] \tag{7}$$

where ξ is a random number uniformly distributed in the interval (0,1).

(*ii*) A particle in the lattice is chosen at random. If the particle is a *B*, then go to (*vi*).

(*iii*) *The selected particle is an A.* If it has at least one NN *A*, then go to (*v*).

(*iv*) The number of NN vacant sites, n_v, is obtained. If $n_v = 0$, then return to (*i*). Otherwise, select a destination site *j* at random among the n_v vacant sites and accept the jump to site *j* with probability $P = n_v P_{di}/P_{tot}$. Return to (*i*).

(*v*) The particle *A* at site *i* has $n_A > 0$ and $n_v \geq 0$. If no one of the n_A pairs *AA* has a *B* particle as an NN, then go to (*iv*). Otherwise, let $n^B{}_A$ be the number of *AA* pairs in conditions to react (with at least one NN *B*) and P_k the probability per unit time of the k^{th} event (the first n_v events are diffusion jumps and the following $n^B{}_A$ events are reactions). Obtain $Q = \sum P_k/P_{max}$ and a random number ξ. If $\xi < Q$, then accept event *k* with probability P_k/P_{max} and return to (*i*). Otherwise, return to (*i*).

(*vi*) *The selected particle is a B.* A diffusion jump is attempted in the same way as done in (*iv*) for particle *A*. The whole process is repeated until no more *A* particles are left on the surface. To smooth fluctuations, thermal desorption runs for a given selection of the parameters are repeated *m* times and averaged spectra are obtained.

Results and Discussion

Our calculations were carried out for $L = 100$, $m = 10$, $E_{r0} = 30$ kcal/mol, $\nu = 10^{13}$ s^{-1}, and $\beta = 10$ K/s. The activation energy for diffusion for each species was varied over a wide interval; however, we found that all significantly different results can be resumed by taking just two values: $E_{dX} = 25$ and 35 kcal/mol ($X = A,B$), corresponding to high and low mobility, respectively. The promoter surface concentration was varied from 0.01 to 0.2, but results for two values are shown as representative: $\theta_B = 0.02$ and 0.2, low and high concentration, respectively. It should be noted that if the distribution of adsorbed species were random, for $\theta_B = 0.02$, on average, 8% of *A* particles would have an NN *B*; alternatively, for $\theta_B = 0.2$, this figure would be 80%. Therefore, in this latter case, on average, every *A* should have at least one NN *B*. This situation can be drastically changed by lateral interactions among adsorbed particles. For *BB* attractive interactions, diffusion leads to the formation of *B* islands that are controlled by the availability of vacant sites produced by the desorption of A_2, thereby decreasing the *AB* interface. In contrast, *BB* repulsive interactions tend to homogenize the distribution of promoters, thereby increasing such interface. On the other hand, *AB* attractive interactions increase the interface, whereas repulsive ones decrease it. Finally, *AA* attractive interactions lead to the formation of *A* islands that are controlled by the availability of vacant sites produced by the desorption of A_2, thereby decreasing the *AB* interface; but, at the same time *AA* attractive interactions may favor the associative desorption, depending strongly on the *B* coverage. The *AA* repulsive interactions have the opposite effect; that is, they favor the formation of the interface but disfavor the associative desorption. These general considerations indicate that the TDS should be strongly dependent on the mobility of adsorbed species and on their interaction energies and will be useful for the interpretation of results.

In what follows, we divide the presentation and discussion of results into three groups: (*i*) no interactions are present among adsorbed species, (*ii*) interactions affect only the activation energy for diffusion, and (*iii*) interactions affect both the activation energies for diffusion and for reaction.

Noninteracting Particles. In Figure 1 we present TDS when no interactions are present among adsorbed particles of any species for different mobilities. From left to right and from top to bottom, we have both species fast,

(27) Binder, K. Monte Carlo Methods in Statistical Physics. In *Topics in Current Physics*, Vol. 7; Springer: Berlin, 1978.

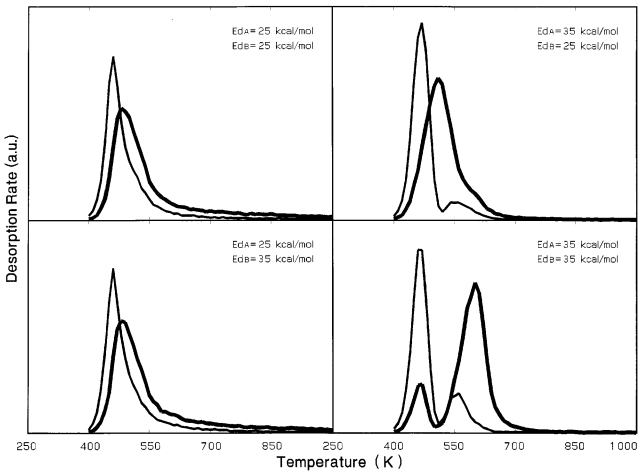

Figure 1. Thermal desorption spectra for the associative desorption of A_2 in the presence of promoter species B for different mobilities of A and B represented by their activation energy for diffusion, E_{dA} and E_{dB}. The case of noninteracting particles ($\epsilon^{XY} = 0$): thick line, $\theta_B = 0.02$; thin line, $\theta_B = 0.2$.

A slow and B fast, A fast and B slow, and both species slow, respectively. This rule is observed throughout in the figures.

Two qualitatively different groups of TDS can be appreciated. The left column, corresponding to fast A mobility, shows mostly expected results: the spectra are single-peaked, the mobility of B is irrelevant, and the peak corresponding to high promoter concentration (thin line) is shifted to lower temperature with respect to the one corresponding to low concentration (thick line).

In the right column, corresponding to slow A mobility, we can see a drastic effect of the promoter mobility, which acts with different intensities at low and high promoter concentrations. The desorption pattern is characterized by two regimes that are evidenced by the appearance of two peaks (for fast B mobility, top, and low θ_B the second one is just a tiny shoulder): a *configurational* (or *contact*) regime, where the AA pairs initially in contact with B react, giving rise to the lower temperature peak, and a *diffusive* regime, where particles must migrate to be able to react, giving rise to the higher temperature peak. By comparing the top and bottom thick-line spectra corresponding to low B concentration, it can be appreciated that the mobility of the promoter species strongly modifies the TDS: for high B mobility, the two regimes mix, giving rise to an almost single-peaked spectrum, whereas low B mobility produces a strong separation in two peaks, with the position of the first coincident with the one corresponding to high B concentration and the position of the second shifted to higher temperature (A particles must diffuse more time to find a B).

Interactions Acting on Diffusion. Here we study the additional effects introduced on TDS when interparticle interactions are taken into account in diffusion jumps.[28]

Figure 2 shows the spectra when only AA interactions are present, for low (a) and high (b) promoter concentrations. For low B concentration, when AA interactions are repulsive ($\epsilon^{AA} > 0$) and the mobility of A is high (left column), the spectra are similar to those corresponding to the noninteracting case, regardless of the mobility of B. This result is due to the interplay between two

(28) In general, given that activation barriers for diffusion and for reaction (chemical recombination) are of a different nature, lateral interactions may act differently on the two elementary processes.

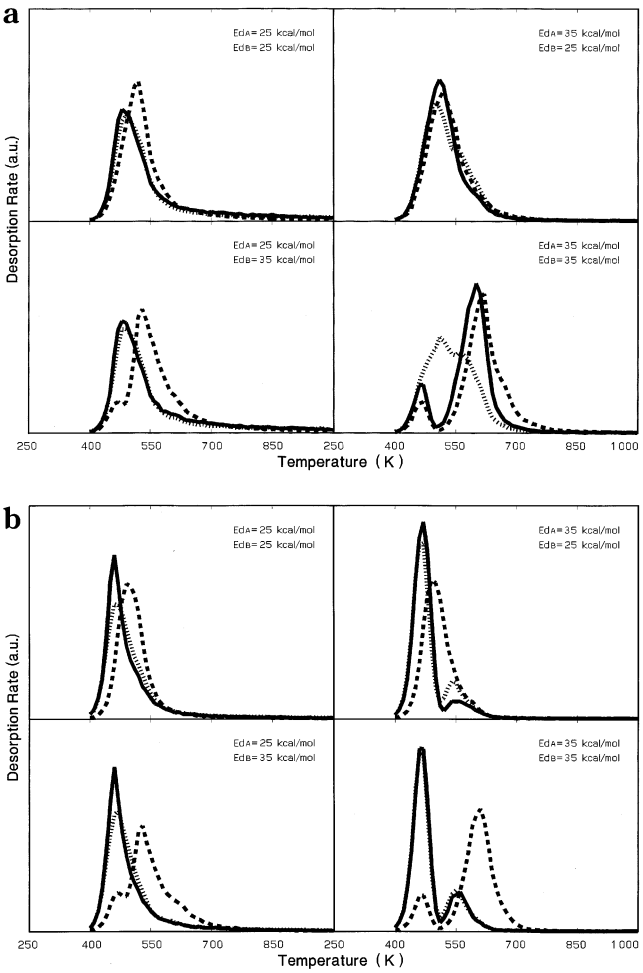

Figure 2. TDS spectra with AA interactions acting on the diffusion energy barrier: solid line, $\epsilon^{AA} = 0$; thin slashes, $\epsilon^{AA} = 2$ kcal/mol; thick slashes, $\epsilon^{AA} = -2$ kcal/mol. (a) $\theta_B = 0.02$. (b) $\theta_B = 0.2$.

mechanisms: on one hand, repulsive interactions disfavor the formation of AA pairs; on the other hand, they increase the mobility of A even more, thus increasing the probability of encounters with B. When the mobility of A becomes low (right column), a second peak appears as a shoulder at high B mobility (top) and the spectrum becomes strongly different from that of the noninteracting case for low B mobility (bottom). Here the contact regime mixes appreciably with the diffusive regime due to the effect of repulsive interactions in increasing the mobility of A. Attractive AA interactions ($\epsilon^{AA} > 0$) produce a general shift of the spectra to higher temperature as compared with the noninteracting case because of the tendency of A to form islands; the major difference is at the left bottom, where the summed effects of A islands formation and low B mobility resolve the contact and diffusive regimes in two peaks.

For high B concentration, repulsive AA interactions practically do not affect the spectra, regardless of the mobility of both species, as compared to the noninteracting case. This result is because the increase in the mobility of A due to repulsive interactions does not contribute substantially to increase the probability of encounter with B given the high concentration of the promoter. For attractive interactions, the spectra are practically the same as for low B concentration. This result is because the formation of A islands segregates the A and B species in macroscopic domains, which makes the AB interface almost independent of the B coverage.

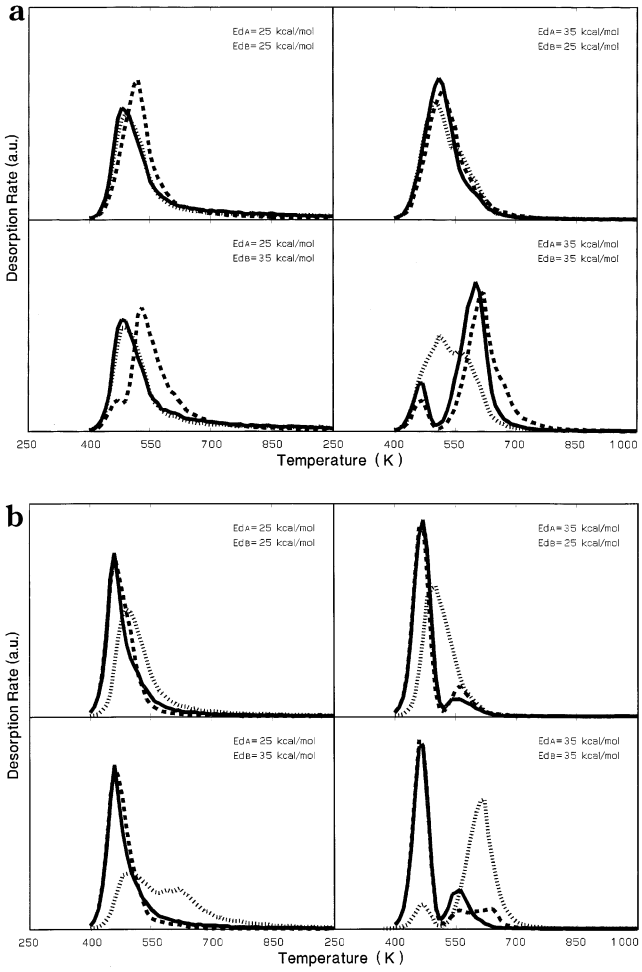

Figure 3. The same as Figure 2 for *AB* interactions.

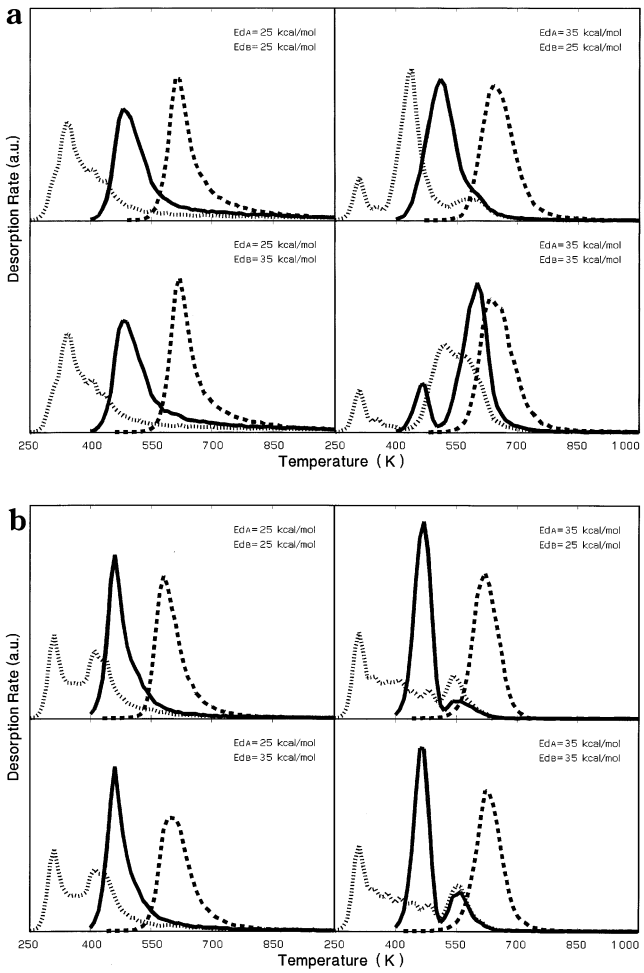

Figure 4. TDS spectra with *AA* interactions acting both on the diffusion and reaction energy barriers. The same conventions are used as in Figure 2.

Figure 3 presents the results when only *AB* interactions are considered for low (a) and high (b) promoter concentrations. These interactions produce modifications of the TDS different from those discussed in the previous case. For low *B* concentration, repulsive *AB* interactions produce double-peaked spectra, except when both species have high mobility and the peaks are shifted to higher temperature as compared to the case of noninteracting particles. This result is a consequence of the fact that now the diffusive regime dominates because the encounter between *A* and *B* is disfavored in all cases and even more when anyone of the two species is slow. The spectra for attractive *AB* interactions, on the other hand, do not differ substantially from those corresponding to the noninteracting case, although the reaction is slightly favored when at least one of the species is fast because, in this case, the increase of the probability of encounters between *A* and *B* becomes the relevant effect.

For high *B* concentration and for repulsive *AB* interactions, the mobility of *B* is the controlling mechanism. If it is fast, it compensates for the lower probability of encounters between *A* and *B* and spectra present a single peak; on the contrary, if it is slow, the diffusive regime predominates and double-peaked spectra are obtained. Attractive *AB* interactions do not produce substantial variations with respect to the noninteracting case, except for a widening of the second peak when both *A* and *B* are slow because, in this case, *AB* interactions contribute to the slowing down of the diffusion process.

BB interactions (not shown) only indirectly affect the TDS. Repulsive interactions produce no visible effects at all because they only contribute to a more homogeneous distribution of promoters. For attractive interactions, the formation of *B* islands is favored. If the concentration of promoters is high, then the spectra are shifted to higher temperature and, if in addition *A* is slow, a second peak develops at high temperature.

Interactions Acting on Diffusion and Reaction. We now consider that lateral interactions modify both the activation energy for diffusion and for reaction. To keep the number of parameters to a minimum, we take $\epsilon^{XY} = \epsilon_r^{XY}$ for all pairs.

Figure 4 shows the spectra when only *AA* interactions are present, for low (a) and high (b) promoter concentrations. As a first general result, just like in the case of noninteracting particles, we see that the spectra are not modified by the mobility of *B* when *A* is fast (left column).

For low *B* concentration, repulsive *AA* interactions produce a general shift of the spectra to lower temperature (because now the effective activation energy for reaction is lower) and multiple-peaked spectra arising from the splitting of the contact peak due to different configurations and the different delays produced on them in the diffusive regime. If *A* is fast, only the contact regime is important, and this gives rise to a spectrum that is a superposition of multiple peaks corresponding to configurations of *AA* pairs having 5, 4, 3, ... NN *A* and 1 NN *B* (these peaks show up as the shoulder on the left at nearly 300 K, the central peak, and the shoulders to its right, respectively). If *A* is slow, the diffusive regime becomes important,

producing a bigger delay on those configurations of *AA* pairs having fewer NN *A*; thus, the different configurational peaks separate more or less depending on the mobility of *B*. If *B* is fast, the peaks corresponding to intermediate configurations are enhanced, resulting in an important central peak. If *B* is also slow, once the *AA* pairs initially with 5 and 4 NN *A* (at nearly full coverage) have been desorbed (first small peak and shoulder), repulsive interactions start to disrupt large *A* clusters and the slow mobility of both species will make a majority of *AA* pairs desorb in configurations with very few NN *A* at higher temperatures (last two big peaks). Attractive *AA* interactions, on the other hand, combines the effects of the formation of *A* islands and the increase in the effective activation energy for reaction to give a single peak shifted to high temperature, with the only effect of lower *A* mobility being that of enhancing the dispersion of the peak, regardless of the mobility of *B*.

Similar considerations apply for high as for low *B* promoter concentration. The difference is that in the case of *AA* repulsive interactions and slow *A* mobility, a purely diffusive peak (*AA* pairs with no NN *A*) appears in exact coincidence with the case of noninteracting particles. This result can be understood by considering that at low *A* coverage and given the high concentration of *B*, encounters of *AA* pairs with a *B* and without other NN *A* are now more probable.

Figure 5 presents the TDS when only *AB* interactions are considered for low (a) and high (b) promoter concentration. The analysis of these results is similar to that corresponding to Figure 3. The main characteristic is that repulsive *AB* interactions make the diffusive regime important even for high *A* mobility. The difference now is that the spectra are shifted to lower (higher) temperature for repulsive (attractive) *AB* interactions given that these interactions decrease (increase) the effective activation energy for reaction.

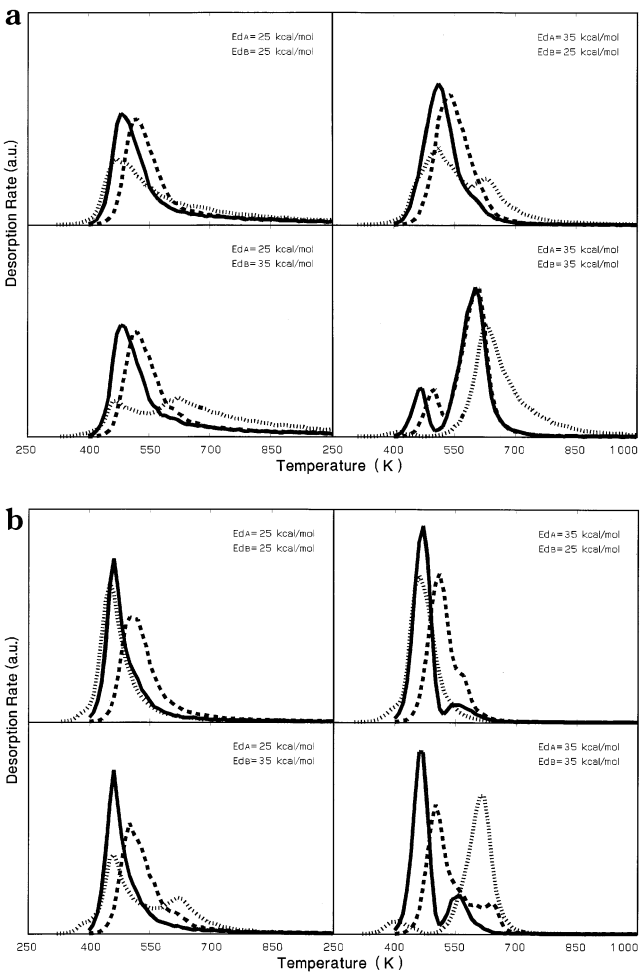

Figure 5. The same as Figure 4 for *AB* interactions.

Conclusions

We have studied by Monte Carlo simulation the kinetics of the associative desorption of species *A* in the presence of a promoter species *B* under nonequilibrium conditions, by analyzing the TDS of the process. A rich variety of behaviors is found, depending on the interplay between the concentration of promoter species, the mobility of species *A* and *B*, and interparticle interactions; these behaviors may act on the energy barriers for diffusion and for reaction. The results can be interpreted in terms of the way in which mobility and interactions facilitate or disturb the formation of the *AB* interface.

Two regimes are found to be present in this process: a configurational, or contact, regime, and a diffusive regime. The importance of each regime in determining the resulting TDS depends mainly on the mobility of species and interparticle interactions. In the case in which repulsive *AA* interactions also affect the reaction energy barrier, the configurational regime gives rise to a multiple-peaked spectrum.

The present analysis may be useful in the design and/or interpretation of experiments involving the kind of process considered here.

Acknowledgment. The present research was carried out with financial support from CONICET of Argentina.

LA991099U