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THE KINETICS OF DESORPTION IN THE PRESENCE OF A GAS PHASE OF THE DESORBING MOLECULE: CO / Re(001)

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TPD/Exchange from CO/Re(001) in a gas ambience showed that the absolute rate of desorption depends on the gas pressure and has a first plus second order rate law. It is proposed that desorption is a two step process from the adsorbed state to a stable intermediate which is itself weakly adsorbed.

Works studying the kinetics of desorption generally do so in an environment that is devoid of a gas phase of the desorbing molecule. This is because most sensitive instruments measure changes in the gas phase and are most effectively used against a zero background. The use of information from such studies in the analysis of reaction systems under normal conditions then makes the implicit assumption that the kinetics of desorption is not explicitly dependent on the gas phase. In recent years, this conventional wisdom, that the kinetics of desorption depends only on surface concentration(s) and is dependent on the gas phase only indirectly, has been challenged by some elegant experiments from Tamaru and coworkers [1–6] on CO/Pd, Rh, Ni. The absolute rate of desorption was found to be made up of two terms, a thermal desorption-rate term independent of the ambience and an "adsorption-assisted" desorption rate term which is an increasing function of the gas phase pressure of CO, i.e., the rate expressions for desorption include an explicit pressure term. The phrase "adsorption" assisted desorption" had been coined to describe this effect which, in mechanistic terms, means that an act of adsorption has, in some way, rendered the act of desorption more probable. A precursor state mechanism has been proposed [7]. The presence of this form of a "pressure gas" has obvious important implications for the analysis of reaction systems.

As long ago as 1970, Klier et al. [8] had reported a pressure effect on surface-adsorbate kinetics. In exchange experiments on the CO/Ni(110) system, the rate of exchange was found to increase with pressure. This phenomenon of a

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pressure dependent exchange rate was then explained by a thermodynamic formulation of the adsorption isotherm in which the saturation coverage was almost directly proportional to the pressure for the pressure range, 10^{-6} to 10^{-3} Torrs, in which their experiments were performed. However, if one incorporates current knowledge of the adsorption isotherms in which the saturation coverages are weakly dependent on the pressure, one can deduce that the exchange rate is explicitly (in contrast to an implicit dependence through the adsorption isotherm) pressure dependent. Yates and Goodman [9] explained an explicit enhancement of the exchange of CO/Ni(100) by gas phase molecules with the suggestion that the presence of gas phase molecules gives a high surface coverage and resulting adsorbate-adsorbate interactions cause some pre-adsorbed labelled molecules to populate lower energy states, thus resulting in a more facile desorption. This experimental observation of a pressure effect has, more recently, been confirmed by Shen et al. [10] who have, in addition, measured kinetic parameters which indicate that the energy of desorption is decreased in the presence of a gas phase, a decrease that is more than is accountable for by the proposal by Yates and Goodman [9]. This led Shen et al. [10] to propose mechanisms in which a weakly adsorbed form of CO is present on the surface when there is a gas ambience or there is a direct energy transfer mechanism from the gas phase molecules to the adsorbed molecules during the displacement process. Shen and Gland [11] further reported the same pressure effect phenomenon for the CO/Pt(111) system and now favor the weakly adsorbed CO mechanism, i.e., the desorption rate enhancement observed in the presence of a gas phase is because then the desorption is from a weakly adsorbed species that only exist in the presence of a gas phase. In yet another, earlier, observation of a pressure effect, Tamm and Schmidt [12] reported rapid isotopic exchange for hydrogen on the W(100) surface. A mechanism where an adsorbed state with a lower binding energy that is in equilibrium with the gas pressure and which mediates the exchange reaction was proposed.

These studies lead to the conclusion that desorption kinetics deduced from experimental set-ups that do not include a gas ambience are not directly applicable for the analysis of reactions under a gas ambience. The proposal by Goodman and Yates [9] gives as the reason the particular chemistry of the adsorbate-substrate system, while the other proposals imply that the phenomenon can be more general. A careful kinetics study should be useful in clarifying the picture. We believe all the explanations heretofore suggested have some elements of truth and here suggest a mechanism for our results that draws upon them for inspiration.

Tamaru and coworkers devised an “isotope jump technique” [1–6] which allows the measurement of the absolute rates of adsorption and desorption while the adsorption reaction was actually proceeding. The technique is a differential method where the absolute rates at the time of change of the gas phase by its isotope are measured by extrapolation. We have modified this into a classical analysis of the surface concentration versus time relationship that evolves during isothermal desorption or exchange (when a gas phase was present), i.e., into an integral approach which can be expected to be more accurate for the study of reaction kinetics. This gives, by curve fitting, the rate equation for the exchange rate. This rate is the absolute rate of desorption, i.e., the absolute value of the rate of the process, forward or reverse, at equilibrium [13]. The situation in an exchange experiment is such that a "high" surface coverage is maintained in contrast to a desorption experiment in which the surface coverage decreases and we might say that the exchange rate measures a desorption rate from a surface that is maintained at a fixed coverage (the saturation coverage at the applied pressure).

CO adsorption on Re(001) has been well characterized by a variety of surface sensitive techniques [14–18]. HREELS shows that at around room temperature, CO is adsorbed only in the linear mode and the CO stretch frequency shows a shift with coverage that is almost entirely due to dipole-dipole coupling [15], i.e., no measurable chemical adsorbate-adsorbate interaction is seen as reflected in the vibrational frequency. Thermal desorption spectroscopy (TDS) [14,18] shows the presence of two well-separated states for an adsorption at room temperature (states are named with the terminology introduced by Ducros et al. [14]), a high energy β-state that is partially dissociated and a low energy α-state that is molecularly adsorbed. TDS shows that at very low exposures, the β-state is first filled and increased exposures result in a simultaneous filling of the α-state and β-state. The TD spectra suggest that changes in the desorption energies of these states with coverage is small. Based on the findings from these studies and our own preliminary work, we decided to study the isothermal desorption and exchange from a saturated surface at 353 K. Under these conditions, desorption would be from the molecularly adsorbed state and the coverage with respect to the number of metal atoms is estimated at 0.3 which puts the adsorbate system in a range where adsorbate-adsorbate interaction, even if it can be present, is unlikely. The TD spectra for a desorption from 353 K is such that any transition to lower energy binding states due to a change in the gas environment is easily discernible.

A study of a Re surface is useful in disclosing the possible generality of the pressure effect phenomenon since Pd, Ni, Rh, Pt and W [1–12] had shown it. Furthermore, Re is a metal of importance in its own right as a component of the reforming catalyst, Pt-Re [19].

The experiments were carried out in a UHV system with a base pressure of 1×10^{-9} Torr and equipped for temperature programed desorption (TPD), AES, LEED, and Ar^+ bombardment for sample cleaning. The chamber is 30.5 l and was pumped by an ion pump with a measured pumping speed of 400 l/s for CO in the 10^{-8}–10^{-9} Torr range so the high pumping speed approximation for a TPD analysis is valid. Thermal desorption was carried out with a temperature programmer operated at a linear heating rate of 8 K/s and the products were analysed with a quadrupole mass spectrometer through simultaneous monitoring of CO^{16} and CO^{18} signals.

The Re(001) sample was cut and polished at the Fritz Haber Institute in Berlin from a boule purchased from Johnson Matthey (UK). This was suspended by spotwelded Ta wires from a rotatable high precision manipulator. The sample was heated by direct heating and its temperature was measured with a chromel-alumel thermocouple spotwelded onto the back face. The sample was cleaned by Ar^+ bombardment for 2 hr, heating in 5×10^{-7} Torr oxygen at 700 K for 1 hr, and finally heating in vacuum at 1200 K for 5 min to anneal and remove the oxygen. Sample cleaniness was verified by AES and TPD. The cleaned sample showed TPD spectra similar to those in the literature [14,18]. The CO^{16} used was of 99.95% purity. The CO^{18} used was purchased from Isotec Inc. (Ohio, USA) with an O^{18} enrichment of 95%. Gas purity was verified with the mass spectrometer prior to use. Gases were introduced by backfilling the UHV chamber via variable leak valves.

Each experimental point in fig. 3 for the surface concentration of CO^{16} left on the surface after exposure of the surface to CO^{18} at a specific pressure, P, and time, t, was obtained by the following procedure. The sample was first flashed to clear the surface. When the sample was steady at the desired temperature (353 K), the surface was saturated by the admission of CO^{16} at a pressure of 2×10^{-8} Torr for 6 min. The flow of CO^{16} was then stopped and CO^{18} was admitted through another leak valve at the desired pressure, P_1, and for a time of exchange, t_1. The flow of CO^{18} was then stopped, the system evacuated for 1 min and the sample heated for TPD analysis. The integral of the TPD spectrum gives the point for t_1 and P_1 in fig. 3. Sample cleanliness was checked from time to time by the TPD spectrum of a saturation coverage at room temperature, and only points bracketed by TPD spectra of a saturation coverage at room temperature that are similar are used in fig. 3.

Figure 1 shows some sample TPD spectra. Figure 1a shows the TPD spectrum from a saturation coverage at room temperature. The agreement with published TPD spectra [14,18] for the same condition is good. Figure 1b shows some sample TPD spectra from those used for calculating data points for P = background of fig. 2 and 3, while fig. 1c shows a series of TPD spectra used for the calculation of the data points for $P = 5 \times 10^{-8}$ Torr in fig. 3. We assume that the UHV background is an approximation to the ideal of an absence of a gas phase of the desorbing molecule, $P = 0$. Adsorption at 353 K populates the α_3- and β-states and exchange is with molecules in the α_3-state. Also, the spectra are such that if a gas ambience causes the population of a lower energy state, i.e., adsorption of CO^{18} from the gas ambience pushes some adsorbed CO^{16} into lower energy states e.g. the α_2- and α_1-states, this would be readily seen. This is not the case for otherwise the spectra for which a gas ambience is indicated would start at a higher CO^{16} background and show some structure in the front of the α_3 peak. A comparison of the spectra of figs. 1b and 1c shows only a very slight shift in the temperature of the peak maxima with total surface coverage of CO (the total, $CO^{16} + CO^{18}$, coverage is different for the cases in the absence and with the

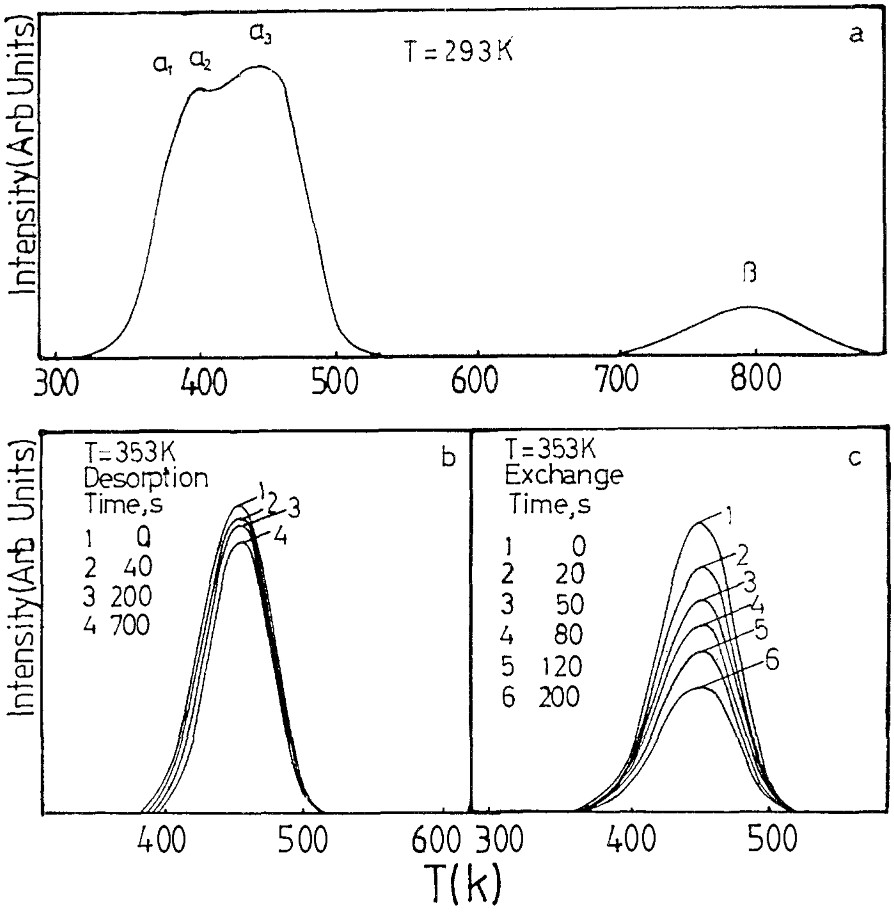

Fig. 1. TPD spectra after saturation adsorption of CO^{16} at (a) room temperature (293 K), (b) 353 K and isothermal desorption at 353 K and under the base pressure of the UHV system for the time indicated, and (c) 353 K and isothermal exchange at 353 K and $P = 5 \times 10^{-8}$ Torr CO^{18} for the time indicated.

presence of a gas ambience). If one assumes that the desorption is a first order process, this implies that there is only a very small variation in the desorption energy with coverage. The peak shapes indicate a first order desorption.

Figure 2 shows data points for $P = 5 \times 10^{-8}$ Torr during the exchange, plotted as $\ln \theta$ versus t and $1/\theta$ versus t. It can be seen that the θ–t relationship can neither be fitted by a first order nor a second order process (with constant desorption energy) since one of the plots should be linear otherwise. We have not considered the case of a variable desorption energy since the surface coverage is constant at the saturation coverage of the applied pressure in the exchange experiment and even if the surface coverage were not constant, other evidence (TPD) peak temperatures and HREELS) indicate that any dependence of the desorption energy, due to adsorbate-adsorbate interaction, on coverage will be

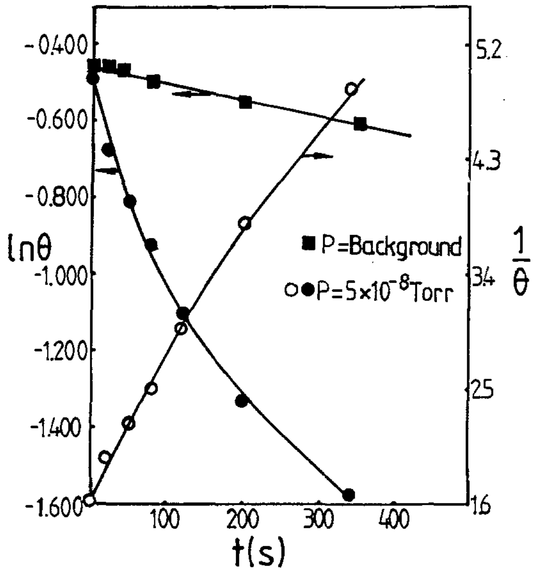

Fig. 2. Ln θ versus t and $1/\theta$ versus t plots for an isothermal exchange in $P = 5 \times 10^{-8}$ Torr CO^{18} at 353 K, and for an isothermal desorption under the base pressure of the UHV system at 353 K.

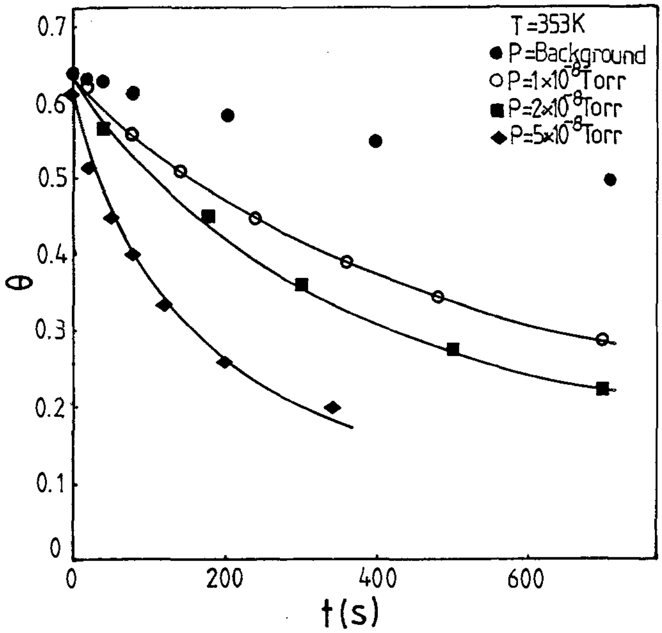

Fig. 3. The change in surface coverage after an exchange reaction of time, t, for exchange reactions carried out under the different pressures of the isotope indicated. Surface coverages are referenced to the coverage at 293 K as the unit. The curves are drawn from a least squares fitting of experimental points to a first plus second order rate law.

Table 1
Apparent rate constants for the first and second order processes as a function of the pressure of CO^{18}

Pressure, Torr	k_1 [a], s^{-1}	k_2 [a], s^{-1}
0	2.7×10^{-4} [b]	
1×10^{-8}	3.0×10^{-5}	2.7×10^{-3}
2×10^{-8}	2.1×10^{-5}	4.3×10^{-3}
5×10^{-8}	1.1×10^{-5}	1.1×10^{-2}

[a] The apparent rate constants, k_1 and k_2, are defined by eq. (4) together with a definition of the surface coverage where the reference is to the saturation surface coverage at room temperature (293 K) as unit surface coverage. The values listed were obtained by least squares fitting to experimental points.

[b] This apparent rate constant was computed from a least square fit to data points with $t > 40$ s and a first order rate law.

small. Similar plots (not shown) for the other points taken with the presence of a pressure indicate that the rate of exchange obeys neither a first nor a second order rate law. The data points for $P =$ background show a straight line in the $\ln\theta$ versus t plot for points with $t > 40$ s implying that desorption under UHV is a first order process as is also indicated by the shape of the TPD peaks.

Figure 3 shows the data points for various pressures in the gas ambience together with a fit of the data points to a first plus second order rate law. The drawn lines are curves computed from the θ–t relationship for a first plus second order process with the apparent rate constants curve-fitted by the least squares difference between experimental and computed points. The optimized rate constants are listed in table 1. This fit is good. The data points clearly show the presence of a pressure effect: the exchange/desorption rates increase with pressure.

The qualitative θ–t relationship in fig. 3 is in agreement with that reported by Shen et al. [10] for CO exchange over Ni(100). The interpretation is different. The optimized rate constants shown in table 1 indicate a mechanism in which the second order rate constant should include an explicit pressure term from which the pressure effect arises. They also require that the first order "rate constants" should decrease with pressure.

The following mechanism is proposed:

$$\begin{tikzcd}
\mathrm{CO(g)} \arrow[r, shift left, "k_d^*"] & \mathrm{CO(ad_w)} \arrow[l, shift left, "k_d"] \arrow[d, shift left, "k_c^*"] \\
& \mathrm{CO(ad_s)} \arrow[u, shift left, "k_c"]
\end{tikzcd}$$

where (ad_w) and (ad_s) signify a weakly adsorbed state and a strongly adsorbed state respectively, and k_c and k_c^* are the rate constants for conversion from the strongly adsorbed state to the weakly adsorbed state and vice versa, and k_d and k_d^* are the rate constants for conversion from the weakly adsorbed state to the gas phase and vice versa. The strongly adsorbed state, (ad$_s$), is the "normal" adsorption state, α_3. The weakly adsorbed state, (ad$_w$), is perceived as a reversibly adsorbed state that adsorbs over the (ad$_s$) state and we assume an adsorption isotherm of the form:

$$\theta_w^T = cP^{1/n}. \tag{1}$$

The superscript, T, denotes that both isotopes are to be counted. This could be a Langmuir isotherm over a limited pressure range. The strongly adsorbed state and the weakly adsorbed state are treated as if they are different phases. We assume that adsorption equilibrium holds during the exchange process and that the coverage by this weakly adsorbed state is not significant under UHV when evacuated for more than a min. The assumption of adsorption equilibrium implies also an equilibrium between the strongly adsorbed state and the weakly adsorbed state, and a Langmuir type equating of the rates of interchange between these two states gives,

$$k_c\theta_s^T(1-\theta_w^T) = k_c^*\theta_w^T(1-\theta_s^T)$$

and allows us to write an "isotherm" relating their concentrations:

$$\theta_s^T = \frac{1}{1+\dfrac{k_c}{k_c^*}\left(\dfrac{1}{\theta_w^T}-1\right)}. \tag{2}$$

When $k_c < k_c^*$, i.e., the number of weakly adsorbed molecules is less than the number of strongly adsorbed molecules, θ_s^T will be only a weak function of pressure through θ_w^T, especially where $\theta_w^T \to 1$.

The experimentally measured quantity is the coverage of the strongly adsorbed state of the originally adsorbed isotope, CO^{16}, and the rate expression for it is:

$$-\mathrm{d}\theta_s^{16}/\mathrm{d}t = k_c\theta_s^{16}(1-\theta_w^T) + k_c^{\#}\theta_s^{16}\theta_w^{18}\theta_s^{16} - k_c^*\theta_w^{16}(1-\theta_s^T) \tag{3}$$

where the superscripts, 16, 18, and T, denote coverage in CO^{16}, CO^{18}, and CO^{16} + CO^{18}, and the subscripts, s and w, denote strong (normal) and weak adsorption respectively. $k_c^{\#}$ is also a rate constant for a conversion from the strongly adsorbed state to the weakly adsorbed state but $k_c^{\#} \neq k_c$ if there is molecule-molecule interaction between the weakly adsorbed state and the strongly adsorbed state that changes the energetics for conversion from the strongly adsorbed state to the weakly adsorbed state. The terms on the right side are arrived at from a mechanism in which desorption is a two step process, and both steps are first order processes. In step 1, a strongly adsorbed species is converted to a weakly adsorbed species, and in step 2, the weakly adsorbed species desorbs. For the physical picture of how a pressure effect can arise, we follow up an idea from Tamm and Schmidt [12]. The desorption of a (strongly adsorbed) species is enhanced by the presence of a weakly adsorbed state when this weakly adsorbed species occupies the empty (strong adsorption) site left behind and prevents return of the original molecule. This is the second term where the concatenation "$\theta_s^{16}\theta_w^{18}\theta_s^{16}$" counts the coverage in strongly adsorbed CO^{16} which has associated weakly adsorbed CO^{18}. The first θ_s^{16} counts "escaped" CO^{16}, θ_w^{18} counts weakly adsorbed molecules that prevents their return, and this is multiplied by (the second) θ_s^{16} since only weakly adsorbed molecules associated with a strongly adsorbed CO^{16} state prevent readsorption of the "escaped" molecule. We assume a 2-dimensional lattice gas model for both the strongly and weakly adsorbed phases in which there is no free translational motion. Experiment indicates that the apparent rate constants of this second order term increase with pressure which preclude a $(1 - \theta_w^T)$ factor. This hints a concerted bimolecular step where a strongly adsorbed CO^{16} acts to displace a weakly adsorbed CO^{18} that moves to occupy the forming vacant site, rather than a sequential process. It is the contribution from an "exchange" between the weakly adsorbed state and the strongly adsorbed state. The first term represents desorption as in vacuum, and under UHV where $(1 - \theta_w^T) \to 1$, and the third term and the second term goes to zero, this dominates and "normal" first order kinetics is seen. The third term represents weakly adsorbed CO^{16} that converts into the strongly adsorbed state.

Equation (3) is expressed in experimentally accessible terms by assuming $\theta_w^{18} \approx \theta_w^T$ during the exchange experiment when the gas is CO^{18} and substituting with the adsorption isotherm, eq. (1) for θ_w^{18}. This assumption also allows us to invoke the steady state approximation for θ_w^{16}, i.e., the concentration in weakly adsorbed CO^{16} is small:

$$\mathrm{d}\theta_w^{16}/\mathrm{d}t = 0 = k_c\theta_s^{16}\left(1 - \theta_w^T\right) - k_c^*\theta_w^{16}\left(1 - \theta_s^T\right) - k_d\theta_w^{16} + k_c^{\#}\theta_s^{16}\theta_w^{18}\theta_s^{16}$$

$$\theta_w^{16} = \left[k_c\left(1 - \theta_w^T\right)\theta_s^{16} + k_c^{\#}\theta_s^{16}\theta_w^{18}\theta_s^{16}\right]/\left\{k_c^*\left(1 - \theta_s^T\right) + k_d\right\}.$$

Substitution with this and eq. (1) into (3) gives

$$-\mathrm{d}\theta_s^{16}/\mathrm{d}t = k_1\theta_s^{16} + k_2\left(\theta_s^{16}\right)^2 \tag{4}$$

$$k_1 = k_c(1 - cP^{1/n})b_p; \qquad k_2 = k_c^{\#}cP^{1/n}b_p; \tag{4a}$$

$$b_p = \left\{1 - \left[k_c^*\left(1 - \theta_s^T\right)\right]/\left[k_c^*\left(1 - \theta_s^T\right) + k_d\right]\right\} \tag{4b}$$

b_p is assumed only a weak function of pressure by the argument following eq. (2).

Equation (4) is the statement of the pressure effect. When $P \to 0$, it gives a first order rate law. For a finite P, it gives a first *plus* second order rate law and when $k_c^{\#} > k_c$, the rate for a finite P exceeds the rate for $P = 0$.

The weakly adsorbed state suggested above is not an observable in our experiments. Our model assumes it is a stable species that, at the temperature of our experiments, desorbs to vacuum in the order of 40 s, and adsorption equilibrium is maintained in the exchange experiments. There is evidence for such species from Shen et al. [11]. Using a technique capable of detecting surface species in a gas pressure (Fluorescence Yield Near Edge Spectroscopy, FYNES), they showed the existence of a reversibly adsorbed species whose population depends on the pressure which has a half-life of the order of 10 seconds under evacuation. In our results, the curve for $P =$ background shows two points for $t < 40$ s that could be construed as indicative of a second order process, i.e., desorption is first plus second order for $t < 40$ s and becomes first order for $t > 40$ s when the population of the weakly adsorbed state becomes insignificant. Our notion of a weakly adsorbed state is different from that species commonly called a precursor state in that the weakly adsorbed state is a stable intermediate rather than a transitory species (a Bodenstein intermediate) to which the quasi-steady state approximation can be applied. However, much of the evidence for the existence of a precursor state [20], namely, a sticking probability that is independent of coverage for a wide range of coverage, can be construed as evidence for a weakly adsorbed state too. The physical difference would be that our postulated weakly adsorbed states lies in a deeper potential well than a physisorbed state, which would imply some attractive interaction between the two adsorbed states.

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