

Entropies of Desorption from Temperature Programmed Desorption Data: Trends and Applications to Rate Constant Determinations

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We show that entropies of desorption can be obtained from temperature programmed desorption (TPD) data. Corrected to the standard pressure of the thermodynamic reference state, these experimentally derived entropies are in general good agreement with Trouton's Rule for which there is theoretical evidence in the literature. Knowledge of these entropies allows the use of the large body of readily available gas-phase thermodynamic data in the determination of the rate constants for surface reactions and allows a more efficient determination of the Arrhenius preexponential factors for surface reactions.

Introduction

Estimates of rate constants for chemical reactions can be obtained in several computational ways: collision theory, activated complex theory,¹ and molecular dynamics^{2–7} are some. Reasonable estimates of reaction rate constants are critical to account for important kinetic effects in reacting systems.

For small molecules on transition metal surfaces, the unity bond index-quadratic exponential potential method (UBI-QEP)^{8,9} has been successfully employed for the estimation of activation barriers. This method requires little computational effort. The UBI-QEP potential energy function has been adapted to molecular dynamics (MD) and statistical mechanical calculations for the purpose of simulating reactions on metal surfaces^{2–7} to yield the Arrhenius preexponential factors. These MD simulations and statistical mechanical calculations seem to give reasonable results;^{2–7} however, they can require significant amounts of computational effort.

The need for an improvement in efficiency can be seen by considering the way in which the MD simulations are carried out to obtain the surface-phase rate constants.^{2–7} To obtain a *zero coverage limit* rate constant that corresponds to an observable quantity, the rate constants are averaged over a set of microcanonical ensembles. Each microcanonical ensemble, having a fixed energy at the outset of the simulation, is composed of several hundred MD reaction trajectories that statistically sample the infinite set of initial conditions (position and velocity) for the reactant(s). Each microcanonical ensemble differs from others in the set of ensembles by the energy of the reactant(s), and there needs to be enough ensembles of trajectories to give a statistical sample of the (infinite) number of possible reactant energies. Since each trajectory can consume several hours of CPU time on a 1000 MHz processor and there can be thousands of trajectories, this type of MD simulation can be computationally demanding. Part of this is because the reaction barriers can be of the same order as the numeric error in the energy. This requires that the algorithm used to solve the equations of motion must control the numeric error to a high degree. Otherwise reaction events will occur, not because of the chemistry, but because of the numeric error in the Newton solver. The goal of the MD simulation is to measure the time required for the reaction events to occur. In our previous works,^{2–7} we have sometimes invested weeks and even months

of computer time in obtaining a single reaction rate constant with the MD method. The MD method is amenable to parallelization; however, many researchers do not have access to highly parallel machines.

Rather than performing MD simulations of both the dissociation and recombination reactions to obtain the rate constants (both preexponentials), it is possible to simulate either reaction (not both) and obtain the preexponential factor for the other from observable gas-phase thermodynamic data employing generally accepted approximations. In earlier work,^{2,3} we employed a similar technique with the difference that we estimated the entropy change of the surface-phase reactions employing statistical mechanical calculations. This seemed to give acceptable results; however, the partition functions needed are accompanied by their own approximations and rely on approximate potential energy functions. The attractive aspects of the present approach is that the ratio of the preexponentials is obtained from experimentally determined thermodynamic data and, to a first approximation, it is independent of the identity of the catalytic metal.

Herein we discuss a method for obtaining Arrhenius-type preexponentials for surface reactions. The ratio of the dissociation and recombination preexponentials is a function of the entropy of the surface reaction, which can be expressed in terms of the gas-phase reaction entropy change and desorption entropies. The ability to obtain the reaction entropies from experimental data allows the use of the large body of gas-phase thermodynamic data in the calculation of surface-phase preexponential factors.

Theory

Consider the Gibbs energy change for a thermodynamically reversible phase-change:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

where the thermodynamic functions have their usual meanings. The change in Gibbs energy that accompanies a reversible phase change is zero so that

$$\Delta H^\circ = T\Delta S^\circ \quad (2)$$

Equation 2 expresses the idea that the entropy change is the “conversion factor” that converts the temperature of the reversible phase change to the enthalpy.

Viewing the desorption process as it occurs in a TPD experiment as an approximation to a reversible phase change with the peak desorption temperature as the approximation to the reversible transition temperature, the TPD estimate of the entropy of desorption at the pressure of the experiment is

$$\Delta S_{\text{des}} = \Delta H_{\text{des}}/T_{\text{des}} \quad (3)$$

The correction to the pressure of the standard state is carried out as follows. The TPD entropy of eq 3 is the difference between the gas-phase and surface-phase entropies:

$$\Delta S_{\text{des}} = S(\text{g}) - S(\text{s}) \quad (4)$$

We consider the surface-phase entropies to be approximately independent of pressure so that the standard entropy change for desorption is

$$\Delta S_{\text{des}}^{\circ} = S(\text{g}) + \int \{\partial S(\text{g})/\partial p\}_{\text{T}} dp - S(\text{s}) \quad (5)$$

In eq 5, the derivative is the partial derivative of the gas-phase entropy with respect to pressure at constant temperature. By Maxwell's relation and the ideal gas equation of state:

$$\Delta S_{\text{des}}^{\circ} = S(\text{g}) - R \ln \{p^{\circ}/p\} - S(\text{s}) \quad (6)$$

where p° and p are the pressure of the standard state (1 bar) and the pressure under which the adlayer desorbs, respectively. Rarely do researchers report the pressure under which the adsorbed layer desorbs; however, 10^{-4} Pa seems to be a common pressure.¹⁰ In the correction of the desorption entropy to standard pressure, we employ this pressure as the lower integration limit. This is a reasonable pressure, and the magnitude of the pressure correction is not at all sensitive to the lower integration limit. Decreasing the lower integration limit, p , in eq 6 by an order of magnitude increases the magnitude of the pressure correction by about 4.5 cal/Kmol. With these pressures, eq 6 becomes:

$$\Delta S_{\text{des}}^{\circ} = \Delta S_{\text{des}} - 41.2 \text{ cal/Kmol} \quad (7)$$

We argue that, for our purposes here, it is not generally necessary to apply a temperature correction to the desorption entropies. First of all, one would often, if not usually, be in the position of applying a temperature correction to the desorption entropies for temperatures that are higher than the equilibrium desorption temperature. This could be determined from the statistical mechanical expression for the Gibbs energy change for desorption at temperatures higher than the equilibrium desorption temperature. However, problems exist with this approach since anytime the Boltzmann distribution is employed, the practitioner has tacitly assumed an equilibrium distribution of thermal energy among the available energy levels. Second, temperature corrections to the entropy of an ideal gas are small for relatively large temperature changes. For example, the temperature correction from, say, 100 to 298 K, is $C_p \ln\{298 \text{ K}/100 \text{ K}\}$, which is 1.1 times the constant pressure heat capacity. This is about 5 cal/Kmol for a monoatomic perfect gas. Also, when modeling chemical kinetics, it is customary to treat the Arrhenius preexponentials as though they are independent of temperature and let the exponential factor describe the temperature dependence.

It is straightforward to show that the ratio of the Arrhenius preexponential factors for the equilibrium: $\text{AB}(\text{s}) \leftrightarrow \text{A}(\text{s}) + \text{B}(\text{s})$ is⁴

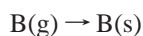
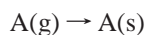
$$\Delta S_{\text{surf}}^{\circ} = R \ln\{A_{\text{diss}}/A_{\text{rec}}\} \quad (8)$$

or

$$A_{\text{diss}} = A_{\text{rec}} \exp\{\Delta S_{\text{surf}}^{\circ}/R\}$$

where A quantities are the Arrhenius preexponential factors for dissociation and recombination and the entropy change is for the reaction as it occurs on the surface. From eq 8, the dissociation Arrhenius preexponential can be obtained from the recombination one and a reasonable estimate of the entropy change for the surface-phase reaction.²⁻⁴

To estimate the entropy change for the surface dissociation reaction needed in eq 8, we employ a thermodynamic cycle:



The sum of the four entropy changes is the entropy change of the surface reaction: For a wide variety of cases, the entropy

$$\Delta S_{\text{surf}}^{\circ} = \Delta S_{\text{d1}}^{\circ} - \Delta S_{\text{d2}}^{\circ} - \Delta S_{\text{d3}}^{\circ} + \Delta S^{\circ}(\text{g}) \quad (10)$$

changes for the gas-phase reactions are available from thermodynamic data in the literature. From eq 10, one sees that it is the part of the sum involving the desorption entropies that constitutes the difference in entropy changes of the gas-phase and surface-phase reactions. We could obtain the desorption entropy changes from MD simulations of the adsorption/desorption processes or statistical mechanical calculations as we have done in the past.²⁻⁴ However, these techniques often require significant amounts of human and computational effort and additional approximations. As is seen below, we employ entropies in eq 10 obtained from TPD data or the corresponding Trouton's Rule. For disproportionation reactions: $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, we use an expression analogous to eq 10 for the entropy change of the surface reaction.

Results and Discussion

Table 1 contains data from TPD experiments (heats of adsorption, peak desorption temperatures) and entropies derived from these data (ΔS_{des} and $\Delta S_{\text{des}}^{\circ}$) for a number of small molecules on various metal, metal oxide, and nonmetal surfaces. The uncorrected desorption entropies cluster around 60 cal/Kmol with the standard desorption entropies clustering around 20 cal/Kmol. We stress that this value of 20 cal/Kmol is the Trouton's Rule value for the standard enthalpy change. We consider this to be experimental evidence of a Trouton's Rule for desorption processes.

The theoretical evidence for the existence of a Trouton's Rule for desorption comes from statistical mechanical calculations and calculations employing constrained dynamics. Sellers and Gislason⁴ have shown with statistical mechanical calculations that the entropies of desorption for a number of small molecules

TABLE 1: Heats of Adsorption ΔH (kcal/mol), Peak Desorption Temperatures, T (K), Entropies of Desorption, ΔS_{des} (cal/Kmol), and Standard Entropies of Desorption, $\Delta S_{\text{des}}^{\circ}$, for Small Molecules on Various Surfaces Derived from Experimental TPD Data

species	surface	ΔH	T	ΔS_{des}	$\Delta S_{\text{des}}^{\circ}$
NO ^a	TiO ₂ (110)	8.4	127	66	25
CH ₃ OH ^b	Ag(111)	9.5	167	57	16
	Ag(110)	9.7	165	59	18
	Cu(111)	12.9	210	62	20
	Pt(111)	11.3	190	60	19
CO ^c	Pt(110)	35.3	560	63	22
CO ^d	MgO(100)	4.1	60	68	27
O ₂ ^e	TiO ₂ (110)	25.8	410	63	22
NO ₂ ^f	Au(111)	14.0	230	61	20
Cl ₂ ^g	Pd(100)	68.0	1100	62	21
CCl ₄ ^h	Si(100)	8.2	132	68	26
propane ⁱ	graphite	7.2	115	62	21
O ₂ ^j	Ag/ α -Al ₂ O ₃	35.6	542	66	25

^a Ref 14. ^b Ref 15. ^c Ref 16. ^d Ref 17. ^e Ref 18. ^f Ref 19. ^g Ref 10. ^h Ref 20. ⁱ Ref 21. ^j Ref 22.

fall into a narrow range. The small molecules in that study⁴ included molecular hydrogen, carbon monoxide, and a number of small hydrocarbons on Ni, Pt, and Pd surfaces. The partition functions for those statistical mechanical calculations employed our potential functions derived from the UBI-QEP method. In addition, Morgner¹² showed with constrained dynamics that methane thiol desorption obeyed a Trouton's Rule. While this theoretically derived evidence is far from complete, it is evidence that the thermodynamics of desorption of a number of small molecules does obey a Trouton's Rule, and it is reasonable that there should be many more such cases.

The Trouton's Rule for desorption processes has some fundamental implications for the ratios of the Arrhenius preexponentials for surface reactions. With the standard desorption entropies clustering about 20 cal/Kmol, one sees from eq 10 that the ratios of preexponentials for surface reactions will be largely independent of the identity of the metal surface. Also, the equation for disproportionation reactions ($A + BC \rightarrow AB + C$) analogous to eq 10 shows that the ratios of preexponentials for the forward and reverse disproportionation are essentially the same as they are for the gas-phase reaction, since the desorption entropy changes will approximately cancel.

In our application of this technique to the determination of the ratio of Arrhenius preexponential factors for surface-phase reactions, we use $\Delta S_{\text{des}}^{\circ}$ values from TPD data as described above when they are available. When they are not available, we use the Trouton's Rule value of 20 cal/Kmol (85 J/Kmol) for the standard entropy of desorption. In this case, for dissociation/recombination reactions eq 10 becomes

$$\Delta S_{\text{surf}}^{\circ} = \Delta S^{\circ}(\text{g}) - \Delta S_{\text{TR}}^{\circ} \quad (11)$$

where $\Delta S_{\text{TR}}^{\circ}$ is the Trouton's Rule entropy change for desorption (20 cal/Kmol or 85 J/Kmol). For disproportionation reactions, the entropy change for the surface reaction is the same as for the gas-phase reaction.

Table 2 contains the standard entropy changes for the surface-phase and gas-phase reactions and the ratios of dissociation to recombination Arrhenius preexponentials for reactions that are

TABLE 2: Ratio of Preexponential Factors (for all transition metal surfaces) and Surface-Phase Entropy Change (cal/K mol) for the Cleavage of the Active Bond

active bond	$A_{\text{diss}}/A_{\text{rec}}$	$\Delta S_{\text{surf}}^{\circ}$	$\Delta S_{\text{gas}}^{\circ}$
H–H	5.2 (0)	3	24
O–O	4.7 (+1)	8	28
O–H	2.3 (0)	2	22
H–OH	1.9 (+1)	6	26
O–CO	1.4(+3)	14	35
S–S	1.4 (+1)	5	26
H–S	1 (0)	0	21
H–SH	1.1 (+1)	5	25
O–SO	3.7(+2)	12	32
S–O	2.6 (0)	5	26

important in sulfur–oxygen–hydrogen chemistry on metal surfaces. The gas-phase entropies are from ref 13. From these data, one sees that the presence of the metal surface has the effect of decreasing the reaction entropy so that the preexponential factors for the recombination reactions are closer in magnitude to the dissociation ones than they are for the gas-phase reactions. Still, the dissociation preexponentials are predicted to be larger than the recombination preexponentials sometimes by several orders of magnitude.

Conclusion

We presented a way of estimating entropy changes for desorption from temperature programmed desorption data. With this approximation, the ratio of preexponentials for surface-phase reactions can be obtained from the large body of available gas-phase thermodynamic data. We show that the standard entropy changes for desorption cluster around a value that is essentially that of Trouton's Rule for the reversible evaporation of liquids.

References and Notes

- (1) Atkins, P.; de Paula, J. *Physical Chemistry*, 7th ed.; W. H. Freeman and Co: New York, 2002.
- (2) Sellers, H. *Surf. Sci.* **2000**, 459, 33.
- (3) Sellers, H.; Anderson, J. *Surf. Sci.* **2001**, 475, 11.
- (4) Sellers, H.; Gislason, J. *Surf. Sci.* **1999**, 426, 147.
- (5) Gislason, J.; Sellers, H. *Surf. Sci.* **1997**, 385, 77.
- (6) Gislason, J.; Sellers, H. *Surf. Sci.* **1998**, 415, 70.
- (7) Gislason, J.; Xia, W.; Sellers, H. *J. Phys. Chem. A* **2002**, 106, 767.
- (8) Shustorovich, E. *Surf. Sci. Rep.* **1986**, 6, 1; Shustorovich, E. *Adv. Catal.* **1990**, 37.
- (9) Shustorovich, E.; Sellers, H. *Surf. Sci. Rep.* **1998**, 31, 1.
- (10) Yang, Y.-N.; Marcos, J. A.; Simons, G. W.; Klier, K. *J. Phys. Chem.* **1990**, 94, 7597.
- (11) Redhead, P. A. *Vacuum* **1962**, 12, 203.
- (12) Morgner, H. *Langmuir* **1997**, 13, 3990.
- (13) Lide, D., Ed.; *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL.
- (14) Sorescu, D. C.; Rusu, C. N.; Yates, J., Jr. *J. Phys. Chem. B* **2000**, 104, 4408.
- (15) Jenniskens, H. G.; Dorlandt, P. W. F.; Kadodwala, M. F.; Kleyn, A. W. *Surf. Sci.* **1996**, 357, 624.
- (16) Fair, J.; Madix, R. J. *J. Chem. Phys.* **1980**, 73, 3480.
- (17) Dohnalek, Z.; Kimmel, G. A.; Joyce, S. A.; Ayotte, P. A.; Smith, R. S.; Kay, B. D. *J. Phys. Chem. B* **2001**, 105, 3747.
- (18) Henderson, M. A.; Epling, W. S.; Perkins, C. L.; Peden, H. F. *J. Phys. Chem. B* **1999**, 103, 5328.
- (19) Bartam, M. E.; Koel, B. E. *Surf. Sci.* **1989**, 213, 137.
- (20) Junker, K. H.; White, J. M. *J. Vac. Sci. Technol. A* **1998**, 16, 3328.
- (21) Zhao, X.; Kwon, S.; Vidic, R. D.; Borguet, E.; Johnson, J. K. *J. Chem. Phys.* **2002**, 117, 7719.
- (22) Busser, G. W.; Hinrichsen, O.; Muhler, M. *Catal. Lett.* **2002**, 79, 49.