Product Energy Distributions and Energy Partitioning in O Atom Reactions on Surfaces.

Bret Halpern and Moris Kori  
Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520

Introduction

Surface reactions involving O atoms are likely to be highly exoergic, with different consequences if energy is channeled mostly to product molecules or surface modes. Thus the surface may become a source of excited species which can react elsewhere, or a sink for localized heat deposition which may disrupt the surface. The vibrational energy distribution of the product molecule contains strong clues about the flow of released energy.

Two instructive examples of energy partitioning at surfaces are the Pt catalyzed oxidations

\[ \text{C}_{\text{ads}} + \text{O}_{\text{ads}} \longrightarrow \text{CO}^* \quad T > 1000 \, ^\circ \text{K} \] (I)

\[ \text{CO}_{\text{ads}} + \text{O}_{\text{gas}} \longrightarrow \text{CO}_2^* \quad T \approx 300 \, ^\circ \text{K} \] (Pt oxide) (II)

We recorded the infrared emission spectra of the excited product molecules and from them determined vibrational population distributions. In reaction I, energy appeared to be statistically partitioned between the product CO and several Pt atoms. In reaction II, partitioning was non-statistical; the CO\textsubscript{2} asymmetric stretch distribution was inverted. In gas reactions these results would indicate a long lived and short lived activated complex, and similar pictures may describe these surface reactions.

The experiments and spectra have been described elsewhere (1,2), so the review given here will be abbreviated. A Pt oxide appeared essential in reaction II; we will discuss evidence for it. We will also estimate the fraction of the released energy that is deposited in the catalyst.

Experimental

All experiments were carried out in a large vacuum chamber pumped at a speed of 10,000 lit/sec. High fluxes of atomic and molecular reactants were directed at a Pt foil, and a steady state flux of vibrationally excited product desorbed into background pressures low enough to avoid vibrational deactivation. Radiation from desorbing product molecules was collected and analyzed in a Fourier Transform Infrared Spectrometer at a resolution of .1 cm\textsuperscript{-1}. The foil temperature, background pressure and reactant flow rates were all under experimental control. The background pressures were adjusted to rotationally cool the emitting species while avoiding vibrational energy loss.

Oxidation of Carbon

Carbon atom targets were supplied by decomposing butane or methane on a Pt foil maintained at \( T = 1000 \, ^\circ \text{K} \) in a simultaneous flux of O\textsubscript{2}. Reaction takes place between adsorbed C and adsorbed O. The relative flow of hydrocarbon and oxygen was adjusted so that the steady state coverage of carbon was low in order to avoid graphite formation. The carbon coverage was sensitively
monitored by measuring thermionic electron emission; a monolayer of C increases emission by a factor of 1000. It did not matter if the O atoms were supplied directly from the gas phase or via dissociatively chemisorbing O₂. This is a consequence of the low C atom coverage; the Langmuir–Hinshelwood mechanism is favored so that the origin of the O atom is not important.

The CO emission spectrum exhibited clearly resolved rotational lines from as high as the seventh vibrational level (1). The derived population distribution, at least for \( v > 2 \), looked nearly Boltzmann, but the plot of \( \ln \) population versus vibrational quantum number had a downward curvature. The "temperature" for this distribution was approximately 4000 \(^\circ\)K, whereas the surface temperature was at most 1400 \(^\circ\)K. The population of \( v = 1 \) was higher than expected from the trend of other levels, and we attributed this to vibrational relaxation via conduction electron excitation prior to CO desorption.

The distribution resembled those observed for the excited CO products in a number of gas phase reactions of an O atom and an organic molecule. By analogy we regarded reaction I as proceeding through a complex of bound C, mobile O and a group of \( n \) Pt surface atoms. Reaction energy \( E \) was randomized in the C-O-Pt complex and partitioned statistically among the various modes of the CO product and the \( s = 3n \) vibrations of the Pt atoms. The distribution of vibrational energy in the product CO is given by a prior distribution \( P_0(v) \) (3)

\[
P_0(v) \propto (1 - \epsilon/E)^s - 1 + \alpha/2
\]

where \( \epsilon = v \hbar \omega \), and \( \alpha = 5 \) is the number of degrees of translational and rotational freedom. A statistical distribution implies that the C-O-Pt complex is sufficiently long lived to assure energy randomization, but is uncoupled from the surrounding Pt surface during the reaction time.

The number of Pt atoms involved in energy partitioning was found by fitting the experimental distribution to the prior distribution for \( v > 2 \). The value of \( E \) is not precisely known, since it must incorporate an uncertain chemisorption energy for carbon as well as an unknown activation energy. For reasonable values of \( E \) from 3 - 5 ev the best fit to the distribution gives \( s \) between 8 and 9. Thus, 2 - 3 Pt atoms strongly share in the released energy, and the distribution of vibrational energy appears to be statistical.

Oxidation of CO

The oxidation of CO on Pt is usually carried out by supplying oxygen as O₂ from the gas phase. Modulated molecular beam experiments have established that it is a Langmuir–Hinshelwood process (4), and infrared emission spectra have shown that the CO₂ product is vibrationally hotter than the Pt catalyst (5). A \( \sim 1 \) ev activation energy is partitioned among the CO₂ product modes and the catalyst. Energy disposal does not favor any internal or translational mode overwhelmingly. There is no evidence for population inversion, and vibrational populations in asymmetric stretch, symmetric stretch, and bending are adequately described by temperatures between 1000 \(^\circ\)K and 2000 \(^\circ\)K. By supplying O atoms directly from the gas phase we make \( \sim 4.1 \) ev available for partitioning. Our object was to find out if the vibrational distribution would be significantly changed, and if so, what change in mechanism was responsible.
The product of Reaction I was a highly excited CO$_2$* molecule (2). There are several singular points of contrast with the conventional CO oxidation. Reaction took place at room temperature, with zero apparent activation energy. The asymmetric stretch emission spectrum was unusual, suggesting a population inversion and high energy content. The room temperature reaction did not proceed on clean Pt but only on Pt that had been heated to 1700 °K and cooled in atomic oxygen. The distinctive features of the excited CO$_2$ emission spectrum are these:

a) Despite a resolution of .1 cm$^{-1}$ the spectrum is diffuse and shifted to lower frequency from the region about 2350 cm$^{-1}$ where the 001 - 000 transition is located.

b) If the background pressure of O$_2$, CO, and O atoms is allowed to rise, a resolved spectrum of CO radiating from v = 1 appears superimposed on the diffuse spectrum. The diffuse CO$_2$ spectrum diminishes in intensity but does not shift.

We interpreted these observations to mean that CO$_2$ desorbed with an inverted vibrational distribution and high energy content. The spectrum is shifted to lower frequency, coincidentally where CO emits, because the inverted distribution gives a preferential occupation of higher levels where anharmonicity has reduced the level spacing. The spectrum is diffuse because in a highly excited triatomic the large number of contributing transitions produces an overlap of rotational lines that overwhelms the resolution.

The CO emission onset at high pressure may be explained as follows. At first sight it might be ascribed to collisions between desorbing CO$_2$ and incoming CO, with a near resonant exchange of vibrational energy. This is unlikely to be so. The desorbing CO$_2$ makes too few collisions between foil and observation zone to permit even near resonant energy transfer. If energy transfer were operative, then the CO$_2$ emission should have occurred from lower levels, rather than merely diminishing in intensity; this was not seen. Collisional energy transfer does not explain the appearance of CO emission. Therefore the CO$_2$ must have been removed by reaction with one of the available collision partners that were present at sufficient concentration. These include the ground states of O, CO, and O$_2$, as well as singlet delta molecular oxygen. There are few reactions which may be written with those reactants that might give a CO product at high yield; the only one which is energetically plausible is

$$\text{CO}_2 + O \rightarrow \text{CO}^* + \text{O}_2^* \quad \text{III}$$

which requires a 2.6 ev activation energy. The only way for reaction III to proceed at room temperature and 10 microns pressure is for the activation energy to be carried in CO$_2$ vibration. (Calculations indicate that translational energy is not effective in driving reaction III.) If that is true then the vibrational energy content of desorbing CO$_2$ must be on the average $\sim$2.6 ev.

The participation of reaction III is the only explanation that is consistent with the observations of CO emission, CO$_2$ destruction, and the improbability of collisional energy transfer. As a consequence we can fix the energy content of the excited product. This is important because the diffuse nature of the emission spectrum makes it difficult to arrive at a unique
distribution of quanta among the three vibrational modes of CO\textsubscript{2}. The constraint on the average energy, however, requires that most of the energy resides in asymmetric stretch, since that mode has the largest vibrational quantum. On that basis we derived the approximate distribution of energy in asymmetric stretch shown in Fig. 1 (2).

![Fig. 1 Asymmetric stretch population distribution of CO\textsubscript{2} from reaction II as a function of vibrational quantum number \(v\). The open circles are derived from the infrared spectrum in reference (2). The closed circles are the distribution according to surprisal theory, Eq. 4, as derived in reference (8). The best fit is found for \(s = 2.5\), so that the number of Pt atoms \(n = 1\).]

The fact that most of the released energy remains in asymmetric stretch may appear surprising given the high level of excitation. Nevertheless it appears that the asymmetric stretch mode in CO\textsubscript{2} is virtually uncoupled from bending and symmetric stretch, which in turn are closely coupled. This has been demonstrated for CO\textsubscript{2} (6,7) at high asymmetric stretch quantum numbers. It is also plausible that the reaction energy is selectively channeled into asymmetric stretch, since formation involves an adsorbed CO molecule and a nearly free O atom.

We also analyzed the derived population distribution using surprisal theory (3,8). The distribution \(P(v)\) resulting from a dynamically constrained, non-statistical partitioning of energy is related to the prior, statistical distribution \(P_{0}(v)\) by

\[
P(v) = A P_{0}(v) \exp \left( \lambda \frac{v}{v_{m}} \right) \tag{2}
\]

Here, \(v_{m}\) is the highest level that is energetically possible, \(A\) is a normalization constant, and \(\lambda\) characterizes the dynamical constraints that distort the prior distribution.

We evaluated \(P_{0}(v)\) for a reaction complex composed of bound CO, a free O
atom, and a cluster of \( n \) surface atoms represented by \( s = 3n \) harmonic oscillators. The reaction product is \( \text{CO}_2 \) with most of its energy in the asymmetric stretch mode. If the product were diatomic, rather than \( \text{CO}_2 \), then the prior distribution \( P_0 \) would be exactly as it was in Eqn. 1. To deal with triatomic \( \text{CO}_2 \) we treat the asymmetric stretch mode as a diatomic molecule, and regard it as the "product" of reaction, since much of the energy is channeled into that mode, and since it is uncoupled from other \( \text{CO}_2 \) vibrations. The symmetric stretch and bending modes are represented by three oscillators (two for doubly degenerate bending), which, like the \( s \) oscillators of the cluster, can share in reaction energy partitioning. The prior distribution \( P_0(v) \) can then be written as

\[
P_0(v) = (1 - \frac{v}{v_m})^s - 1 + \frac{\alpha}{2} + 3 = (1 - \frac{v}{v_m})^s + \frac{9}{2}
\]

where again, \( \alpha = 5 \). The asymmetric stretch distribution \( P(v) \) then becomes

\[
P(v) = A \left(1 - \frac{v}{v_m}\right)^s + \frac{9}{2} \exp\left(\frac{\lambda v}{v_m}\right)
\]

For an exoergicity of 4.1 ev the highest level is \( v_m = 16 \), and the best fit of Eqn. 4 to the experimental distribution is found for \( \lambda = 15.2 \) and \( s = 2.5 \). The theoretical and experimental distributions are shown in Fig. 1. The value of \( s = 2.5 \) means that \( n \sim 1 \), so the number of catalyst atoms involved in energy partitioning is small. In contrast to reaction I, energy partitioning in reaction II is highly non-statistical, and one expects a smaller fraction of released energy to appear in the Pt cluster.

**Discussion**

We comment on two aspects of reactions I and II. The first is the requirement that Pt be heated in \( \text{O} \) atoms to promote reaction of atomic \( \text{O} \) and \( \text{CO} \) at room temperature. The second is the partitioning of energy to the solid.

The formation of an oxide layer can have several effects. It provides a surface that is "saturated" with oxygen, so that \( \text{O} \) atoms can only be weakly bound. The energy \( E = 4.1 \text{ ev} \) available for product vibration is then higher than in the Langmuir-Hinshelwood \( \text{CO} \) oxidation. The oxide layer separates the vibrationally excited \( \text{CO}_2 \) product and the underlying conduction electron gas; this reduces loss of vibrational energy via electron-hole pair excitation during the brief \( \text{CO}_2 \) residence time. There is some evidence from high vacuum studies that a silicon impurity within the bulk is required to bind oxygen. That may be true in our work, but our high \( \text{O} \) atom flux would in any case favor the formation of \( \text{PtO}_2 \). It is of interest to find other indications of oxide layer formation under conditions similar to those in our infrared experiments. We have done this recently in a fast flow system at 1 torr pressure by means of a novel "chopped fast flow" technique (9).

Chopped fast flow is an adaptation of molecular beam chopping to study heterogeneous kinetics by exploiting the high reactant and product fluxes available in low pressure fast flow systems. In this technique, a catalyst surface is exposed to reactant square waves in a steady carrier flow and the transient response of a surface coverage or a reaction product is monitored. In the experiment of interest, we generated a 5 Hz square wave of \( \text{O} \) atoms by using a "vibrating needle" gas source (9) to direct a small \( \text{O}_2 \) flow either
into a microwave discharge or to a line bypassing the discharge. The 0 and 0₂ that periodically left the discharge flowed downstream to a hot Pt filament (1300 °K < T < 1800 °K). The Pt filament was thus exposed to a square wave of 0 atoms and 0₂ at low concentration in 1 torr of an inert carrier gas. In addition, the filament was exposed to a steady flow of pentane that did not pass through the discharge. Pentane decomposes on hot Pt to give chemisorbed carbon, which is removed by the adsorbed 0 atoms supplied either by 0 or 0₂. The rise and fall of carbon coverage was tracked by monitoring thermionic emission with an electrometer whose output was fed to an oscilloscope.

Suppose that the microwave discharge is not activated. If carbon is present on the filament, and the 0₂ square wave turns "on", carbon will be oxidized and the emission current will drop. As soon as the 0₂ turns "off", impinging pentane will quickly give rise to a monolayer of carbon, and the emission current will increase. The key point is that the desorption time of remaining chemisorbed oxygen is ~ 2 microseconds at T = 1500 °K. When the oxygen is off, the Pt filament instantly has sites available for pentane adsorption and decomposition; the emission current rises immediately and reflects the prompt buildup of a carbon monolayer. This is seen in Fig. 2.

![Diagram of C₆H₁₂ and timing diagrams](attachment:image.png)

Fig. 2 The top two curves are timing diagrams of the 0 atom 5 Hz "chopped" fast flow and steady pentane flow. The lower curves are oscilloscope traces of the response of the thermionic emission current j to carbon coverage formation and removal by 0₂ or 0. When 0 atoms are present, the buildup of carbon, and thus the response of j, is delayed until the oxide layer has decomposed.

The sequence is different when the microwave discharge is activated. Then 0 atoms as well as 0₂ strike the filament in the "on" cycle; carbon is removed and the emission current is low. In the "off" part of the cycle, however, one observes that the onset of carbon deposition, and therefore of emission current, is delayed. If the 0 atom concentration is increased by increasing the microwave power, the delay becomes longer, as seen in Fig. 2. Evidently reaction of 0 atoms with Pt at high temperature generates an oxide layer that
decomposes or evaporates relatively slowly. This oxide layer does not catalyze the decomposition of pentane; carbon deposition is then delayed until the oxide disappears and makes available sites on bare Pt. In this way these transient experiments support the idea that reaction of Pt with O atoms at high temperature results in a layer stable at lower temperature.

The fraction of energy $E_s/E$ appearing in the catalyst is of practical and fundamental interest. In reaction I, the CO vibrational distribution was consistent with a statistical partitioning of energy, so we estimate $E_s$ on that basis.

If the diatomic product CO had very closely spaced vibrational levels, and the Pt cluster is treated as a collection of s loosely coupled oscillators, then the average energies $E_t$, $E_v$, $E_r$, and $E_s$ of CO translation, vibration, rotation, and Pt cluster vibration would stand to each other in a ratio given by an equipartition argument as $3/2 : 1 : 1 : s$. The fractions in each mode would then be given by

$$
\frac{E_t}{E} = \frac{3/2}{s + 7/2} \quad \frac{E_v}{E} = \frac{E_r}{E} = \frac{1}{s + 7/2} \quad E_s/E = s/(s + 7/2) \quad [5]
$$

However, the CO vibrational levels are widely spaced; the average energy in vibration is given by a sum over the prior distribution:

$$
E_v/E = \frac{\sum (v/v_m)(1 - v/v_m)^s + 3/2}{\sum (1 - v/v_m)^s + 3/2} \quad [6]
$$

The calculation of the remaining fractions involves integration over densities of states and summations over the CO vibrational levels. The results are

$$
\frac{E_t}{E} = \frac{3/2}{R/(s + 5/2)} \quad \frac{E_r}{E} = \frac{R}{s + 5/2} \quad E_s/E = sR/(s + 5/2) \quad [7]
$$

where $R$ is given by

$$
R = \frac{\sum (1 - v/v_m)^s + 5/2}{\sum (1 - v/v_m)^s + 3/2} \quad [8]
$$

For the values of $s$ and $v_m$ in the range of interest here, $R$ is about .9. In the limit as $v_m$ tends to infinity, the fractions in Equ. 7 become equal to those for continuous diatomic vibrational levels in Equ. 5. In fact, plots of the various fractions versus the number $s$ of oscillators are very similar for the cases $v_m = 16$ and $v_m = \infty$. The main difference is that $E_v/E$ is less than $E_r/E$ in the case of widely spaced levels, rather than equal to it.
as for continuous levels. Thus the fraction of energy appearing in the catalyst for reaction I can be approximated by

\[ \frac{E_s}{E} = \frac{s}{s + 7/2} = .72 \]  

since \( s = 9 \) for a cluster of 3 Pt atoms. The value found from Equ. 7 is only slightly larger. Because \( \frac{E_s}{E} \) is so high, it is of interest to determine the probability that sufficient energy can accumulate in one oscillator to induce evaporation or diffusion. We will present the results of that calculation as well as the details leading to Equ. 7 in a future paper.

In reaction II energy disposal was non-statistical. The average energy in \( \text{CO}_2 \) asymmetric stretch was fixed at roughly 2.6 ev on chemical grounds so that the fraction of energy left for distribution to all other modes is \( 1 - \frac{2.6}{4.1} = .365 \). This fraction is to be divided among \( \text{CO}_2 \) translation and rotation, the three oscillators corresponding to bending and symmetric stretch, and the \( s = 2.5 \) oscillators of the catalyst. If this is done statistically, then the fraction of the energy appearing in the catalyst oscillators during reaction II is given by

\[ \frac{E_s}{E} = .365 \frac{s}{s + 11/2} = .11 \]  

As expected, this is much smaller than in reaction I.

References

7) D. Bailly, C. Rossetti, and D. Guelachvili Chemical Physics 100 101 (1985)

Acknowledgements

The authors are thankful for the support of the National Science Foundation grant CPE-8114348, Petroleum Research Fund PRF 17006-AC5-C, and Air Force grant OSR F499620-80-C-0026.