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CO₂ PRODUCT VELOCITY DISTRIBUTION FOR CO OXIDATION ON PLATINUM. (U)

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6 CO₂ PRODUCT VELOCITY DISTRIBUTIONS FOR CO OXIDATION ON PLATINUM

9 Journal articles

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It has been inferred^{1,2} from the very peaked ($\cos^5 \theta$) angular distribution of the CO₂ formed by catalytic oxidation of CO on Pt (111) that the product CO₂ is desorbed with excess translational kinetic energy. We report here the first direct measurement of the CO₂ velocity distributions and angular distributions for this reaction on polycrystalline Pt. These quantitatively confirm the inference: For example the most probable CO₂ energy is 3560° K, perpendicular from Pt at 880° K.

The experiment was performed in an ultra-high vacuum system equipped with a rotatable doubly differentially pumped mass spectrometer detector and a quadruply pumped molecular beam source. Further details of the apparatus have been given elsewhere.³ A collimated (1° FWHM) supersonic molecular beam with kinetic energy $E/k = 980$ K mechanically chopped into pulses of approximately 21 microseconds FWHM

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hit a polycrystalline Pt foil. The Pt was maintained at temperatures between 300° K and 1100° K in oxygen atmospheres of 5×10^{-8} to 5×10^{-6} torr. The peak CO pulse intensity was approximately 10^{15} / cm^2 / sec at the surface, with a duty factor of 1%. The surface had been cleaned by standard techniques.⁴ Auger electron spectroscopy of the cleaned Pt indicated only oxygen and calcium (5 - 10%) as surface contaminants. Because the system was pumped with a very small, 11ℓ/sec, ion pump when oxygen was applied, the surface oxygen was not substantially depleted due to reaction with ambient CO.⁵ Ion pump conversion of O₂ to CO produced a CO/O₂ ratio of less than 1/1000 in the chamber.

Fig. 1 shows distributions of the time elapsed from the point at which the CO pulse reaches the sample position to the time the indicated species is ionized (14.45 cm away). 1 (a) characterizes the CO beam when allowed directly into the detector. 1 (b) and (c) characterize the residence plus flight time of CO₂ product emitted at angles of 0° and 45° (specular) from the surface normal, with a surface temperature $T_s = 880^\circ \text{K}$ and an average O₂ pressure of 1×10^{-7} torr. As discussed further below, there is a regime of surface temperatures and O₂ pressures for which residence time is negligible compared to flight time. The data shown in figure 1 were obtained under such conditions and thus directly give velocity distributions. Any disregarded residence time would only increase the inferred CO₂ velocity. For CO₂ desorbing in the normal direction the most probable velocity was 1.16×10^5 cm/sec, implying a kinetic energy of $E/k = 3560^\circ \text{K}$. At larger

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angles from the surface normal the most probable velocity decreases monotonically. At 45° it is 9×10^4 cm/sec for a kinetic energy of $E/k = 2140^\circ$. When transformed to number density velocity distributions the data show speed ratios (FWHM/most probable velocity) of $.88 \pm .12$ and $1.11 \pm .23$ for the desorption at 0° and 45° from the normal respectively. The speed ratio for a thermal distribution is 1.155. Both results are qualitatively similar to the results of Comsa et al for H_2 desorption from a sulfur contaminated nickel surface.⁶

As surface temperatures are lowered progressively from 650 to 425 K the elapsed time distributions become increasingly broader with a tail to long times. For example, for O_2 pressure of 3×10^{-7} torr, Pt at 428 K, the decay time of the tail is 464 μ sec. As the temperature is raised above approximately 650° K the width of distributions is essentially independent of temperature (and the peak shifts progressively to shorter times). The results below 650° K show decay times thought to be characteristic of surface diffusion of reactants.⁵ Further evidence for this effect was that higher ambient O_2 pressures gave sharper distributions in the lower temperature regime. This diffusion limited behavior is characteristic of the Langmuir-Hinshelwood reaction mechanism.

The present velocity distributions are remarkably narrow for a polycrystalline sample. The decrease of velocity with angle from normal is inconsistent with a unique 1-dimensional barrier model such as proposed by van Willigen⁷ which gives the opposite trend. Nevertheless it is possible that a diversity of reaction sites and hence barriers could produce the observed trend: High barrier high velocity products would be concentrated at small angles and low barrier low velocity

products would be spread to wider angles where they would be preferentially observed. Clarification of the applicability of a barrier model awaits further experiments with single crystal samples.

Previous molecular beam studies of this reaction had shown sharply peaked number density angular distributions. Palmer and Smith¹ reported $\cos^d \theta$ with d ranging from 4 to 6, for various (111) samples studied. Employing a barrier model,⁷ Palmer² interpreted these results as implying a barrier to adsorption for CO_2 of 7 kcal/mole (3500° K). This result is comparable to our finding a peak kinetic energy of 3650° K for desorption in the normal direction (at $T_s = 880^\circ\text{K}$). For our polycrystalline sample we find d values of 2 to 3. The discrepancy in d cannot be attributed simply to the distribution of surface normals for the various exposed faces. Helium scattering from this sample showed a FWHM of 18° implying a FWHM distribution of surface normal directions of 9° , and convoluting this distribution with a $\cos^6 \theta$ distribution reduces the exponent d to only 5.75.

Acknowledgment

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Figure Caption

Fig. 1) Elapsed time distributions (and with subtraction of background) at ambient Oxygen Pressure = 1×10^{-7} torr, $T = 880^\circ \text{K}$: a.) CO beam, b.) CO_2 product at 0° from normal, c.) CO_2 product at 45° from normal. Flight path = 14.45 cm.

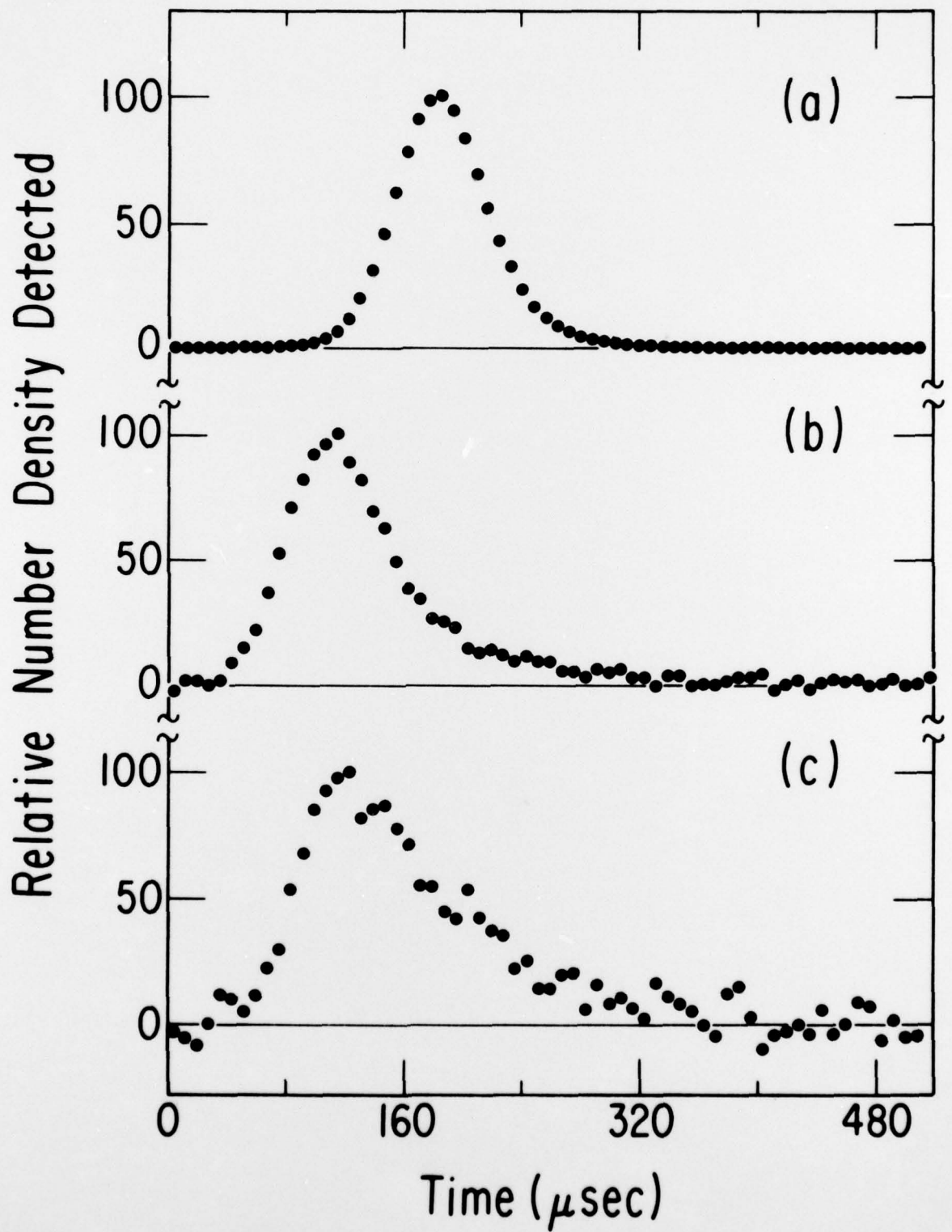


Fig.1

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