On the basis of the Auger data of Fig. 2, at least 40% of the saturation coverage of oxygen must adsorb before O₂ desorption is observed. Thus, it appears that competition between two modes of oxygen depletion occurs during thermal desorption of oxygen: Desorption into the bulk and desorption as molecular oxygen, with desorption being the predominant depletion mode at low coverages.

Conrad et al.² have also reported evidence for dissolution of oxygen into the bulk of Pt(111).

Analysis of the oxygen thermal desorption data, assuming second order kinetics, yields values of $56 \pm 2$ kcal/mol and $2.5 \times 10^{-3}$ cm$^2$ s$^{-1}$ for the activation energy of desorption and the preexponential factor of the desorption rate coefficient, respectively, in the limit of zero coverage. At nonzero coverages the desorption data are complicated by contributions from multiple states and/or interadsorbate interactions. A value for the initial sticking probability of 0.2 was determined from the Auger data shown in Fig. 3, where the constant rate of desorption at exposures below 2 L implies a mobile precursor model for oxygen adsorption at $T \leq 170$ K.

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Abstract: Chemisorption of oxygen on the (110) surface of iridium

D. E. Ibbotson, J. L. Taylor,² and W. H. Weinberg²

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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The chemisorption of oxygen on Ir(110) has been investigated under ultrahigh vacuum conditions with thermal desorption mass spectrometry (TDS), contact potential difference measurements, Auger electron spectroscopy, and LEED. Oxygen may adsorb in three distinct chemical states: a molecularly chemisorbed species that is stable below 100 K, a dissociatively chemisorbed species, and a surface oxide that forms rapidly above 700 K.

The oxide layer saturates at a coverage of 0.25 ML (1 ML = $9.6 \times 10^{14}$ atoms/cm$^2$) and forms with an estimated activation energy of 45 kcal/mol, assuming first order kinetics and a preexponential factor of $10^{12}$ s$^{-1}$. Two forms of the surface oxide are observed, a disordered phase and a ordered phase which corresponds to a (1 X 4) LEED pattern. Both forms exhibit identical chemical properties. Formation of the oxide layer through thermal activation causes the total saturation coverage to increase from 1 ML on the clean surface to 1.25 ML on the oxidized surface, as evidenced from TDS.

Different LEED patterns of dissociatively chemisorbed oxygen are observed on clean and oxidized Ir(110). A $p(2 \times 2)$ structure forms on the clean surface near 0.25 ML coverage, whereas a $c(2 \times 2)$ structure forms on the oxidized surface near 0.5 ML. Thermal annealing is necessary to order the $c(2 \times 2)$ in the [001] azimuth with an energy of diffusion of 47 kcal/mol, assuming first order kinetics and a preexponential factor of $10^{12}$ s$^{-1}$. Slow ordering of the $p(2 \times 2)$ in the [001] azimuth at 300 K is observed on the clean surface with an estimated diffusion energy of 20 kcal/mol, again assuming the same kinetics as above.

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³National Science Foundation Predoctoral Fellow.
⁵Alfred P. Sloan Foundation Fellow. and Camille and Henry Dreyfus Foundation Teacher-Scholar.
Oxygen desorbs molecularly from Ir(110) with an activation energy of 45–70 kcal/mol, decreasing continuously with increasing coverage. The adsorption kinetics are described by a second-order precursor model for surface temperatures between 300 and 700 K. The difference between the activation energies for the desorption and diffusion of the precursor in this model is 2.1 kcal/mol. Oxygen chemisorption is not activated since the initial sticking probabilities on the clean and oxidized Ir(110) surfaces are equal to 0.28 and 0.4, irrespective of the surface temperature. The dipole moment and polarizability of dissociatively chemisorbed oxygen have been calculated from contact potential difference measurements and adsorption kinetics for clean and oxidized Ir(110). The dipole moment and polarizability change at 0.25 ML coverage on the clean surface and at 0.5 ML coverage on the oxidized surface. These changes are associated with the completion of overlayer structures, noted above, and a shift in binding site from chemisorption on top of the rows at low coverages to chemisorption between the rows at high coverages on the clean and oxidized surfaces. Although the dipole moment for any coverage is independent of temperature, the polarizability is inversely proportional to temperature.

A third chemical state of oxygen that is stable below 100 K is inferred from contact potential difference (CPD) measurements. If an overlayer of oxygen that is chemisorbed at 90 K is annealed to 300 K, the CPD changes irreversibly indicating that oxygen may chemisorb molecularly below 100 K. No evidence for desorption is observed. The activation energy for the dissociation of molecular oxygen is 8 kcal/mol, whereas the desorption energy is at least 10 kcal/mol. This cannot be associated with diffusion since the activation energy for diffusion is 20 kcal/mol in the [001] direction and 1 kcal/mol in the [110] direction. On clean and oxidized Ir(110), the dipole moment (per atom) of molecular oxygen is equal to that of dissociatively chemisorbed oxygen in the low coverage state on the respective surfaces. This suggests that molecular oxygen chemisorbs with the molecular axis parallel to the surface and occupies two adjacent sites above the topmost row of surface atoms.

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***Alfred P. Sloan Foundation Fellow, and Camille and Henry Dreyfus Foundation Teacher-Scholar.