The hydrolysis of IIIb therefore provides the first example of a change in rate-determining step in the hydrolysis of a vinyl ether.[12]

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[12] It should be pointed out that Kankaanperä has recently investigated the hydrolytic behavior of a related substrate, 2-ethoxy-2,3-dihydropyran: A. Kankaanperä, *Acta Chem. Scand.*, 23, 1465 (1969). On the basis of a slightly inverse solvent isotope effect, solvent isotope effects in H_2O–D_2O mixtures, and activation parameters, he concluded that this substrate hydrolyzes by *concurrent* acetal and vinyl ether pathways (Schemes I and II). Unfortunately, no buffer experiments were reported, and a firm decision regarding the hydrolysis mechanism of this material must await further work now in progress in our laboratory.

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Electron Spectroscopy of Platinum–Oxygen Surfaces and Application to Electrochemical Studies

Sir:

Several papers have recently appeared[1,2] where the authors discuss the electron distribution for a variety of platinum compounds *via* observed shifts in core electron binding energies. ESCA is a powerful technique for studying the surface properties of metals and already shows promise as a tool in elucidating mechanisms of heterogeneous catalysis.[1] In this study we wish to report direct spectral observation of chemisorbed oxygen on a platinum surface and to report binding energies for oxides produced from chemical oxidation of the platinum substrate. In addition, these results will be applied to the investigation of an electrochemically perturbed platinum electrode in an attempt to more clearly elucidate the types of oxides which are observed. Although the spectral measurements cannot be performed in the electrochemical cell the unequivocal chemical identification of electrochemically formed surface compounds would aid tremendously in interpreting the corresponding current–potential behavior.

The large ionization cross section for the Pt 4f electrons as well as the natural conductivity of platinum yield very high counting rates with a minimum of experimental complexity. Sample pretreatment consists either of etching a 0.5-cm² platinum foil with hot aqua regia, followed by (a) reduction with hydrogen at 400° or (b) reduction with $FeSO_4$. All cleaned platinum samples for the 4f($^5/_2$) and 4f($^7/_2$) lines exhibit a distinct asymmetric shape slanted toward high binding energies and the peak area ratios deviate from the theoretical value of 1.33. Delgass[1] suggested that the low ratio for a prereduced platinum foil was due to platinum oxide on the surface. This effect has also been observed for platinum which has been vapor deposited within the sample chamber at 10^{-5} Torr.[3] Pure PtO_2 has symmetric 4f bands with the proper peak area ratio of 1.33. Siegbahn[4] and Clark[2b] have reported symmetric Pt 4f bands in numerous platinum complexes. Pure gold, on which oxygen is not strongly adsorbed, has very symmetric 4f bands with a peak area ratio of 1.33 using our spectrometer. Thus, the platinum surfaces have two chemical environments for the Pt, and using unskewed gaussian shapes, we could resolve the spectra into two distinct sets each with the 1.33 ratio (see Figure 1a). Coupled with the presence of a strong and symmetrical O 1s peak (half-band width 1.5 eV) at 531.8 eV[5] and the known tendency of oxygen to rapidly chemisorb on the clean platinum surface,[6] the second species (see Table I for binding energies) is undoubtedly due to chemisorbed oxygen. Note that for physically adsorbed oxygen, a doublet O 1s band would be expected due to the paramagnetic character of molecular oxygen.[7] We have always observed the presence of a C 1s band on the platinum surface although

Table I. Binding Energies in Electron Volts for Oxidized Platinum Surfaces[a]

	Nitric acid treatment[b]		Half-band widths	Rel peak
A	4f($^7/_2$)	4f($^5/_2$)	4f($^7/_2$)	areas, %
Pt	70.7	74.0	1.2	41
PtO_{ads}	71.8	75.1	1.9	39
PtO	73.4	76.6	1.3	14
PtO_2	74.2	77.5	1.2	6

	Electrochem treatment[c]		Rel peak areas at		
B	4f($^7/_2$)	4f($^5/_2$)	+0.7 V[d]	+1.2 V	+2.2 V
Pt	70.7	74.0	56	39	34
PtO_{ads}	71.6	74.9	39	37	24
PtO	73.3	76.6	<5	24	22
PtO_2	74.1	77.4	0	0	20

[a] Spectra obtained on a Hewlett-Packard Model 5950A using monochromatic Al X-rays. Bands resolved on a Du Pont Model 310 curve resolver. [b] Refluxed for several hours in concentrated HNO_3. [c] 1 *M* $HClO_4$. [d] Oxidation potential held at indicated potential for 3 min; freshly reduced electrode is taken before each run.

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[1] W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catal. Rev.*, 4, 179 (1970).

[2] (a) C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 93, 1904 (1971); (b) D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Commun.*, 601 (1971).

[3] J. Lester, Northwestern University, private communication.

[4] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Harmin, G. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA; Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Boktryckeri AB, Uppsala, 1967, p 25.

[5] All binding energies are reported with respect to graphite, C 1s, as 284.0 eV. The half-band widths for the $^7/_2$ and $^5/_2$ bands were assumed to be equal for the first deconvolution. Then the half-band widths were adjusted to obtain the best fit. In general the $^7/_2$ band was about 0.1 eV narrower. In the complex spectra (as Figure 1c) the peak ratio was held at 1.33 to complete the deconvolution. The metallic platinum bands on the pure surface are fit by a lorentzian shape a bit better than by a gaussian shape; however, the nonmetallic platinum oxides have gaussian band shapes.

[6] D. O. Hayward and D. M. W. Trapnell, "Chemisorption," Butterworths, London, 1964.

[7] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Bear, "ESCA Applied To Free Molecules," North Holland, Amsterdam, 1969, p 56.

the more drastic cleaning procedures minimize the magnitude of this peak. Nominally, the count rate is an order of magnitude below the chemisorbed oxygen count rate.

The binding energies for the various oxides of platinum could be determined from known samples. For example, PtO is prepared by partial oxidation of platinum foil exposed to oxygen (15 atm) at 300°.[8] The binding energies for the 4f electrons are shifted to 73.4 and 76.6 eV. The values for $PtO_2 \cdot H_2O$ (Adam's catalyst) are further shifted to 74.5 and 77.8 eV in excellent agreement with the shifts reported by Delgass.[1] With known spectra for four platinum species, the spectra for chemically oxidized surfaces can be readily interpreted. For example, data in Table I illustrate the resolved spectrum for a nitric acid oxidized substrate. Known values of binding energies for Pt, PtO_{ads}, and PtO are used in the deconvolution while the value for the PtO_2 species is determined from the best fit.

The electrochemically formed oxides are prepared potentiostatically in 1 *M* $HClO_4$ using a surface pretreated *via* aqua regia followed by $FeSO_4$ reduction. After several minutes of electrolysis, the electrode is removed from the cell, rinsed thoroughly in nitrogen-saturated distilled water, and immediately placed in the ESCA sample chamber. Binding energies for the electrochemically formed oxides could be determined from the sequence of spectra shown in Figure 1. For example, Pt and PtO_{ads} peak values can be obtained in Figure 1a. Using these values in Figures 1b and c the remaining binding energies can be found and compared to knowns for chemical identification. These results are given in Table I. For each of the four species, the peak area ratios for Pt 4f ($^5/_2$) to 4f ($^7/_2$) are near 1.33. Note that at the +1.2 V oxidation potential, both Pt and chemisorbed oxygen are observed, in general agreement with many oxidation mechanisms.[9] Above +1.6 V, the relative concentration of PtO_2 begins to increase until it becomes the predominate species at +2.2 V. These results conclusively reveal the presence of discrete stoichiometric platinum oxides on the electrode surface and represent the most definite spectroscopic evidence yet available to confirm their existence.

ESCA is clearly a valuable tool for examining in a semiquantitative manner the composition of complicated thin films. The direct observation of chemisorbed species along with binding energy shifts of surface substrates may yield the intricate details regarding electronic reorganization in the bonds. Comparison of ESCA data to other results, especially low-energy electron diffraction[10] data, may further aid in understanding chemisorption. In addition the technique appears directly applicable to chemically analyzing electrodes which have been electrochemically altered or covered with electrogenerated reaction products. Further studies regarding these items are in progress.

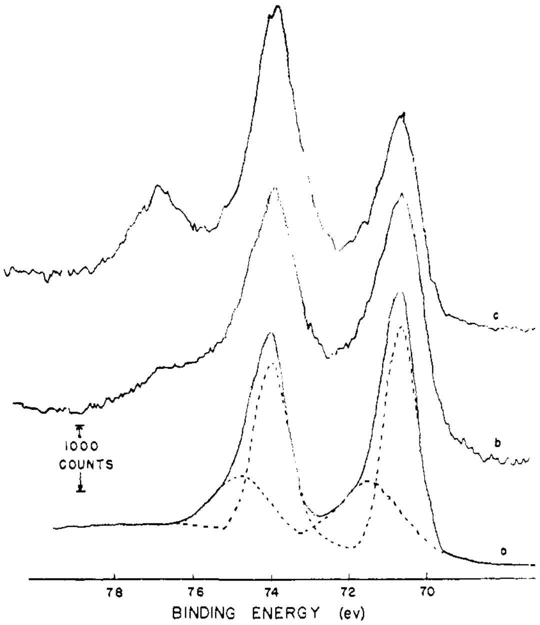

Figure 1. Platinum 4f electron spectra of platinum foil pretreated *via* (a) hydrogen reduction at 400° for 10 hr and hydrogen desorption at 400° (10^{-5} mm) for 5 hr followed by adsorption of pure oxygen (1 atm) at ambient temperature, (b) electrochemical oxidation at +1.2 V, and (c) +2.2 V *vs.* sce in 1 *M* $HClO_4$. Curves b and c have been displaced upward.

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(10) J. W. May, *Advan. Catal.*, 21, 152 (1970).

A Thermochemical Probe into the Mechanism of Electrophilic Addition to Olefins

Sir:

Most of the evidence concerning the mechanism of electrophilic addition to olefins, particularly bromination, has come either from kinetic measurements[1] (substituent effects) or from product analyses[2] (stereochemistry and regiospecificity). However, it has proved difficult to obtain unequivocal evidence about the nature of the cationic intermediates (or the transition states which precede, and presumably closely resemble them). For a long time such additions were considered to be generally stereospecific and trans, which was explained in terms of the well-known cyclic bromonium ion intermediate proposed by Roberts and Kimball,[3] but it is now clear that polar bromine additions can show quite variable stereoselectivity, ranging all the way from predominant cis to exclusive trans addition.[4] Thus, the nature of the intermediates has been shown to depend strongly on the structure of the starting olefin, and it is now more

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(1) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Elmsford, N. Y., 1966, pp 114–128, and references cited therein.

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