The Effect of Rhodium Environment on Oxidation Mechanism: Conversion of Norbornene to Norbornanone on Rh(111)-p(2×1)-O

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We have recently discovered an unusual class of olefin oxidation reactions on Rh(111)-p(2×1)-O.[1-4] Oxygen chemisorbed on Rh(111)-p(2×1)-O adds to styrene[2] and propene[3] to afford their respective methyl ketones and to isobutene to form *tert*-butyl alcohol.[4] On the basis of isotopic labeling data, we proposed that oxygen directly adds to the 2-carbon, yielding the oxametallacycle,[3] which is analogous to several organometallic complexes.

Recently, McMillan et al. have proposed a cationic intermediate for the oxidation of olefins, including propene, styrene, and norbornene on an oxide-bound rhodium complex, (alumina)Rh-(O_2).[5] They further proposed that the cationic species collapses to an alkyl dioxide that rearranges to a ketone enolate via β-proton transfer.[5]

This study was undertaken to test for a cationic intermediate on Rh(111)-p(2×1)-O, since its reactivity appears to be similar to that of (alumina)Rh(O_2). Skeletal rearrangements are a diagnostic for a cationic intermediate.[5-8] For example, skeletal rearrangements have been reported for norbornene oxidation on an alumina-bound Rh complex[5] and by metalloporphyrins.[6] Similarly, the isomerization of *exo*-2,3-epoxynorbornane to 3-cyclohexene-1-carboxaldehyde is acid catalyzed.[7]

All experiments were performed in an ultrahigh-vacuum chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr.[9] The Rh(111)-p(2×1)-O has an oxygen coverage of 0.5 monolayers and was prepared by exposing clean Rh(111) to dioxygen at 300 K.[3] The nearest and next nearest oxygen–oxygen distances are 2.69 and 4.66 Å, respectively, on Rh(111)-p(2×1)-O.

Norbornanone is produced from norbornene oxidation on Rh(111)-p(2×1)-O (Figure 1). There is no detectable 3-cyclohexene-1-carboxaldehyde, the skeletal rearrangement product. The norbornene oxidation product is unambiguously identified as norbornanone on the basis of mass spectral data (Table I).

Norbornene is also hydrogenated to norbornane and combusted to CO, CO_2, and H_2O in the temperature range 400–600 K. The CO and CO_2 evolutions are typical for oxidation of hydrocarbon fragments on rhodium.[3,4] Dihydrogen is also evolved. Norbornene desorbs at 230 K for exposures >15 s, and multilayers sublime at 170 K for exposures >30 s, defined as saturation.

The rate of norbornanone evolution is probably limited by desorption. The norbornanone peak is asymmetric and centered at 290 K during oxidation of norbornene (saturation exposure) on Rh(111)-p(2×1)-O. The norbornanone product peak varies from ~370 K at low exposures to ~290 K as the exposure approaches saturation. Similarly, norbornanone desorbs from Rh(111)-p(2×1)-O at ~370 K for low exposures, shifting gradually to 290 K with increasing exposure. Some norbornanone also combusts to CO, CO_2, and H_2O.

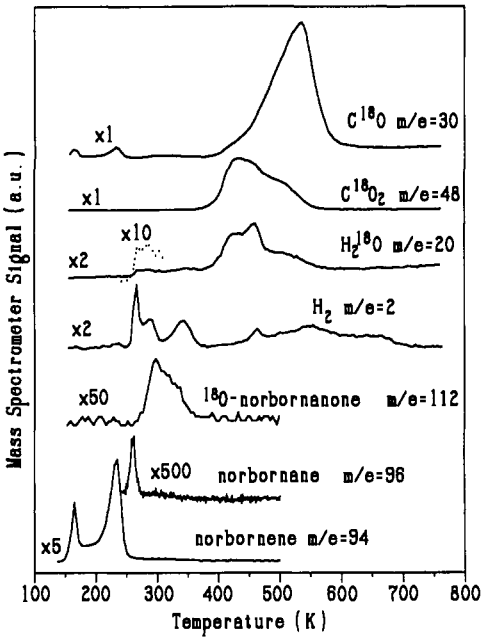
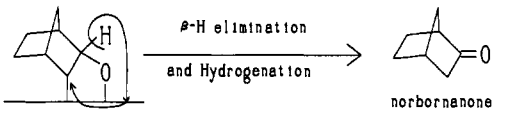
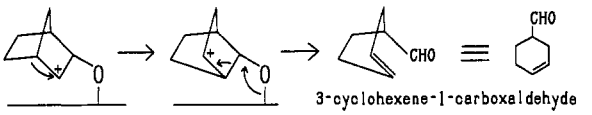


Figure 1. Temperature-programmed reaction of norbornene on Rh(111)-p(2×1)-^{18}O. Norbornene is exposed to Rh(111)-p(2×1)-^{18}O for 30 s at 130 K (heating rate of 10 K/s). Products are monitored at their parent ions.

Scheme I



Scheme II



X-ray photoelectron spectra show that oxygen adds to norbornene below 250 K on Rh(111)-p(2×1)-O. An O(1s) peak with a binding energy of 531.9 eV, in the range characteristic of alkoxides and carbonyls,[10] emerges after heating to 250 K. There is no detectable difference between the Rh(3d) spectra of clean Rh(111) and Rh(111)-p(2×1)-O because the bulk signal obscures the signal from the surface.

Table I. Relative Intensities for Fragments of Norbornene Oxidation Products on Rh(111)-p(2×1)-O and Related Molecules

molecules	relative intensity of *m/e*										
	110	95	92	91	81	79	68	67	66	41	39
norbornene oxidation product	13	0	0	0	11	12	20	100	100	90	100
norbornanone	15	1	1	2	13	10	19	100	98	93	96
exo-2,3-epoxynorbornane	10	21	28	44	71	84	10	51	100	71	130
3-cyclohexene-1-carboxaldehyde	30	16	35	47	45	100	8	35	20	65	98

(1) We previously reported styrene oxidation. Recalibration of the oxygen coverage showed that styrene selective oxidation to acetophenone occurs on Rh(111)-p(2×1)-O with an oxygen coverage of 0.5, not on Rh(111)-p(2×2)-O.[2]

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The product distribution for norbornene oxidation on Rh(111)-p(2×1)-O is consistent with the oxametallacycle intermediate, Scheme I. If a cationic intermediate were formed, it should rearrange to 3-cyclohexene-1-carboxaldehyde on a rapid time scale (Scheme II).[5,6,8,11]

Furthermore, acetone is the sole product of propene oxidation on Rh(111)-p(2×1)-O. A cationic intermediate should afford propanal because of the greater stability of the secondary cation that would be produced from oxygen attack at the 1-position.[12] Steric considerations favor acetone formation for an oxametallacycle intermediate.[3,13]

Epoxidation followed by rearrangement to the norbornanone is likewise ruled out. No norbornanone is detected during reaction of *exo*-2,3-epoxynorbornane on Rh(111)-p(2×1)-O.[14] By ruling out epoxidation, the differences in the oxidation chemistry of Rh(111)-p(2×1)-O and Ag are demonstrated. Norbornene is epoxidized to 2,3-epoxynorbornane by oxygen chemisorbed on Ag(110).[15] The underlying reason for the difference between silver and rhodium is not understood but may be related to their respective abilities to break and form C–H bonds, since norbornanone formation requires a 2,1-hydrogen shift whereas epoxidation does not require any migration of hydrogen.

The difference between the oxide-bound Rh complex and the Rh(111)-p(2×1)-O surface is a clear example of substantially different reaction mechanisms for extended metal surfaces and smaller clusters. The differences in particle size and Rh oxidation state or the presence of acidic sites on the alumina may lead to the different reaction paths on the supported material. Although the supported Rh complex is not well-characterized, an oxidized mononuclear rhodium compound has been proposed.[16] The Rh is nearly zero-valent on Rh(111)-p(2×1)-O since there are no measurable chemical shifts in the Rh(3d) binding energies, although the surface contribution may be difficult to detect. Shifts of 1–2 and 2–4 eV are expected for Rh(I) and Rh(III), respectively. Furthermore, the presence of molecular O_2 on the Rh center was postulated.[5,16] If, indeed, O_2 is present, it could lead to different reactivity; it is clearly not present on Rh(111)-p(2×1)-O. The relative stabilities of ions and radicals may also be different in the vicinity of an extended, conductive surface than when in contact with a cluster containing a few metal atoms due to screening of the charge by the metal conduction electrons. The screening may affect both the time scale and energetics for skeletal rearrangement. Additional information about the supported Rh catalyst and theoretical modeling are necessary to better address these issues.

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(10) For example, *tert*-butoxide has an O(1s) binding energy of 530.5 eV on Rh(111)[17] and acetone a binding energy of 531.6 eV on Rh(111)-p(2×1)-O.[18]

(11) It is possible that the rate of norbornanone formation is much more rapid than rearrangement on the extended metal surface than on supported clusters.

(12) McMillan et al.[5] proposed that a glycolate intermediate is formed during propene oxidation on (alumina)$Rh(O_2)$. No acetone is formed from 1,2-propanediol on Rh(111)-p(2×1)-O in preliminary studies; thus, this pathway is excluded.

(13) Addition to the 1-position of a terminal alkene would bring the alkyl group into close proximity to the surface, creating repulsive interactions. This assertion is supported by the substantially lower oxidation yields of internal compared to terminal olefins.[19]

(14) Temperature-programmed reaction of *exo*-2,3-epoxynorbornane on Rh(111)-p(2×1)-O produces CO, CO_2, and H_2O above 350 K, along with *exo*-2,3-epoxynorbornane desorption at 210 and 300 K. No other products are detected.

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Antibody-Catalyzed Double Stereoselection in Fluorinated Materials

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Recent years have seen breakthroughs in the development of enzymes[1] and/or enzymelike catalysts[2] for asymmetric induction. In particular, molecular recognition by antibodies[3,4] has attracted the interest of synthetic chemists. A class of chiral compounds with multiple stereocenters, namely, diastereomerically pure fluorinated materials, used to differentiate biological properties,[5] has attracted intense interest. To date their preparations have required the separation of diastereoisomeric mixtures or the stereoselective synthesis of fluorinated compounds, both of which may be problematic.[5,6] Therefore, we sought to determine whether it is possible to isolate four optically pure stereoisomers in the maximum 25% yield by direct optical resolution of a diastereoisomeric mixture by an antibody. We have examined the antibody-catalyzed separation of 1,2- or 1,3-diastereoisomeric mixtures, i.e., the possibility of separating each of the four stereoisomers in high optical purity (>97–99% ee).

Enzymelike catalyst design (antibody reagent design) requires the preparation of haptens with structures that would mimic the site of catalytic activity, through transition-state analogues. To form the desired antibody reagents, an immunogenic conjugate was prepared by reaction of a phosphonate, **4**, with a carrier protein (bovin serum albumin and keyhole limpet hemocyanin).[7] To effect the separation of four stereoisomers, four stereochemically related haptens bearing a fluorine atom and a methyl group

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(7) Lymphocytes from the spleen of BALC/c mice immunized with each type of the purified antigens (the BSA–phosphonate conjugate or the KLH–phosphonate conjugate) were fused by standard protocols using mouse myeloma cells (P 3-X 63-Ag.8. U-1) as the fusion partner. Antibodies were screened by ELISA for cross-reactivity with the BSA–hapten conjugate, i.e., for inhibition of binding to the BSA–hapten conjugate by free hapten. Six or eight antibodies were obtained for each diastereomer. Antibodies were purified from ascites fluid by protein A Sepharose 4B affinity chromatography and were determined to be >95% homogeneous by sodium dodecyl sulfate polyacrylamide gel electrophoresis.

(8) The antibody (40 μM, Lowry assay, with a molecular weight of 150000 for immunoglobulin G) was incubated at 25 °C in 60 mL of phosphate buffer at pH 7.3. The racemic ester (10 mM) in acetonitrile (6 mL) was hydrolyzed for 15 h at 25–27 °C in this solution. The antibody was removed by Centricon filtration; the mixture was acidified with 1 N HCl, and then the oily materials were extracted with diethyl ether. After determining the hydrolysis ratio by ^{19}F NMR signal intensities, the carbinol and benzyl ester were separated by column chromatography on silica gel.

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