transient absorption was observed upon direct excitation of the azoalkane **3b**. At azoalkane and benzophenone concentrations of (3.1–6.5) × 10^{-3} and (1.9–3.8) × 10^{-3} M, more than 90% of the 351-nm radiation was absorbed by benzophenone. Triplet benzophenone (λ_{max} = 530 nm) was rapidly quenched by energy transfer to the azoalkane, k_{et} = (2.5 ± 0.2) × 10^9 M^{-1} s^{-1}. Biphasic decay curves, which fitted well to a dual exponential function, were observed at 320 nm, and the faster decay rate was equal to that of triplet benzophenone. The slower component of 1 μs is attributed to the decay of triplet **2b**, the lifetime of **2b** being 1 order of magnitude less than that of parent **2a** (Table I). The decay rates of the triplet biradicals **2a** and **2b** at various temperatures gave linear Arrhenius plots from which the activation parameters E_a and A were calculated (Table I).

Another example for the effect of dimethyl substitution on the lifetime of triplet biradicals is available from two separate studies of the perinaphthadiyls **5a** and **5b**,[11,12] which have so far not been considered from this perspective. Fisher and Michl[11] have determined the decay rate of **5a** in solid polyethylene at 10–140 K; the linear segment of their Arrhenius plot above ~120 K extrapolates to a lifetime of ca. 25 ms at 20 °C. To check this huge extrapolation, we generated **5a** by benzophenone-sensitized flash photolysis of naphthocyclopropane in degassed acetonitrile. The observed transient absorption had a sharp peak at 338 nm, characteristic for **5a**. The decay of **5a** was dominated by second-order contributions over the first two half-lives (first $t_{1/2} \approx$ 10 ms), which shows that the intrinsic (first-order) lifetime must be considerably longer (≥25 ms) under these conditions. The Arrhenius parameters for **5b** were determined in the range of −35 to 0 °C, with glycerol as a solvent to avoid second-order contributions.[12] The extrapolated lifetime of about 400 μs at 20 °C is in agreement with the first-order contribution to the decay of **5b** observed in less viscous solvents (benzene, acetonitrile). Again, the lifetime of the dimethyl derivative **5b** is at least 50-fold shorter than that of parent **5a**.

Thus the 1,3-biradicals **1**, **2**, and **5** consistently show a massive enhancement in the rate of triplet–singlet intersystem crossing (isc) resulting from the seemingly "innocuous" 2,2-dimethyl substitution. What is the reason for this remarkable effect? Structural differences between the **a**/**b** pairs, e.g., diminished delocalization of the unpaired electrons in **2b** as a result of the "buttressing" effect of the geminal methyl substituents, are unlikely to be responsible for the increase in isc rates, as the zero-field parameters D, which are a measure of the average distance between the unpaired electrons in triplets, are very similar in each pair (Table I).

The counteracting effects of through-bond and through-space coupling[13] are nearly balanced in the nonbonding orbitals of **1a**.[14] Dimethyl substitution gives rise to enhanced through-bond coupling, as is easily seen by Heilbronner's method.[15] This will increase the energy gap between the essentially nonbonding orbitals, lower the energy of the singlet state relative to the triplet ground state, and hence lower the energy barrier for isc.[16] Moreover, the increased difference between the energies of the nonbonding orbitals results in a greater weight of ionic contributions in the lowest singlet state wave function and hence leads to faster isc, as predicted by rule 2 of Salem and Rowland.[17] The first effect (reduced energy gap) is expected to lead to a decreased activation energy E_a for isc, while the second (increased spin–orbit coupling) should affect mainly the preexponential factor A in the biradical decay rates. Similar arguments should apply to the pairs **2a**/**2b** and **5a**/**5b**, although the experimental Arrhenius parameters (Table I), taken at face value, suggest that reasoning by analogy may be an oversimplification.[18]

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(18) The activation energy E_a of **5b** is somewhat *higher* than that of **5a**, but this is overridden by a rather dramatic increase in the A factor. In view of the large difference in the conditions used to determine these Arrhenius parameters (Table I), we hesitate to consider these subtleties as significant. Furthermore, it should be recalled that the decay process of **5a** is a 2,1-hydrogen shift[11] and *not* ring closure as in **2a**, **2b**, and **5b**.

Selective Oxidation Reactions on Rh(111)-p(2×2)-O: The Conversion of Styrene to Acetophenone

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We report the unprecedented partial oxidation of an alkene to the corresponding methyl ketone by oxygen chemisorbed on Rh(111)-p(2×2)-O under ultrahigh vacuum conditions. We find that styrene ($C_6H_5C(H)=CH_2$) reacts with atomic oxygen on Rh(111)-p(2×2)-O to form acetophenone ($C_6H_5C(=O)CH_3$) during temperature-programmed reaction. To our knowledge, this is the first observation of olefin partial oxidation to form a ketone on Rh(111)-p(2×2)-O. Indeed, we have found that several alkenes are oxidized to the corresponding methyl ketones by oxygen on Rh(111)-p(2×2)-O, suggesting that this is a general process.[1]

The catalytic oxidation of alkenes is of extreme industrial importance since selective oxidation products serve as starting materials in the production of many specialty chemicals and polymers.[2] The reactions that we have discovered are unprecedented and proceed by a mechanism that is distinctly different from other oxidation systems. In particular, we find that allylic C–H bond activation does *not* control oxidation kinetics and selectivity on Rh(111)-p(2×2)-O.

All experiments were performed in an ultrahigh vacuum chamber, using crystal preparation and cleaning methods described in detail previously.[3] Temperature-programmed reaction data for multiple masses were obtained by using a computer-controlled UTI 100-C quadrupole mass spectrometer. The Rh(111)-p(2×2)-O surface was prepared by exposure of the initially clean Rh(111) to 1 × 10^{-8} Torr of dioxygen for 2 min at 300 K. A sharp (2 × 2) low-energy electron diffraction (LEED) pattern was observed after this procedure, and a single O(1s) peak with a binding energy of 529.5 eV was observed in the X-ray photoelectron spectrum. Styrene (99%) and styrene-d_8 (98% D) were obtained from Aldrich, dried by using CaH_2, and used without further purification.

Gaseous acetophenone is evolved in a peak centered at 275 K, with a small tail extending to 370 K, during temperature-programmed reaction of styrene on Rh(111)-p(2×2)-O (Figure 1). The selectivity for acetophenone evolution is estimated to be ~40%, based on a comparison of the integrated C(1s) X-ray photoelectron intensity at 250 K and 350 K. Similarly, the yield of acetophenone is estimated to be 0.025 molecules/Rh atom by using these data and the integrated O(1s) intensity of the (2×2)-O

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Table I. Fragmentation Patterns for Styrene Oxidation Product and Several Possible Geometric Isomers

molecule	intensity at m/e											
	122	120	107	105	92	91	77	65	51	45	43	39
oxidation product[a]	–	18	–	72	–	–	100	–	76	–	35	–
^{18}O-labeled oxidation product[a]	18	–	67	–	–	–	100	–	75	30	–	–
acetophenone[a]	–	20	–	75	–	1	100	4	77	–	38	–
phenylacetaldehyde[a]	–	13	–	1	24	100	3	38	20	1	1	43
styrene oxide[a]	–	13	–	2	27	100	10	43	30	4	9	50
dihydrobenzofuran[b]	–	100	–	1	15	70	1	8	7	–	–	
vinyl phenyl ether[b]	–	100	–	–	8	73	21	12	16	–	–	
tolualdehydes[b]	–	83	–	1	11	100	1	30	20	1	1	

[a] Measured in our laboratory spectrometer. [b] Taken from the literature.[5]

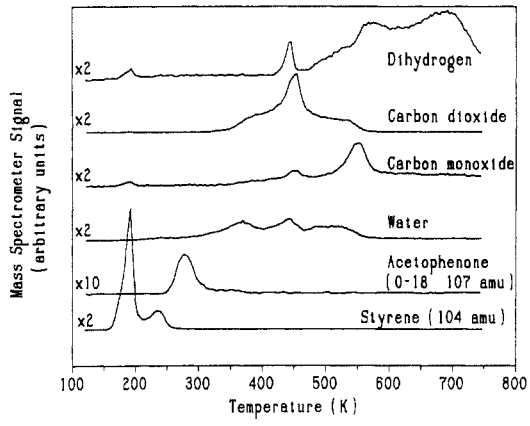

Figure 1. Temperature-programmed reaction of styrene multilayers on ^{18}O-labeled Rh(111)-p(2×2)-O. The heating rate was constant and ~10 K/s. The adsorption temperature is 130 K, and the styrene exposure corresponds to ~1.5 times that required for styrene multilayer desorption. [^{18}O]Acetophenone is detected at m/e = 107 while all other products were monitored as their parent ions.

overlayer. These estimates are subject to error of ±15% due to the difficulty in separating styrene desorption from acetophenone evolution.

Styrene that does not react desorbs at 190 K (multilayer) and 240 K. In addition, the combustion products water, carbon dioxide, carbon monoxide, and dihydrogen are produced. Water and carbon dioxide are evolved with similar kinetics in three peaks at 360, 450, and 510 K. CO is primarily evolved at 550 K. Some dihydrogen desorption is also observed above 500 K. At low exposures of styrene, no styrene or acetophenone evolution is observed; only CO, CO_2, and H_2O are produced.

The parent ion was determined to have m/e = 120 since it was the highest mass detected. All ions up to m/e = 130 were examined in a series of three experiments, each of which covered a 50-amu mass range. The parent ion mass is increased by 2 amu due to the addition of one ^{18}O atom when styrene is reacted on Rh(111)-p(2×2)-^{18}O; m/e = 122 is observed but not m/e = 124 or m/e = 120 (Table I). These data demonstrate that the product has C_8H_8O stoichiometry.

The oxidation product was unequivocally identified as acetophenone on the basis of a comparison of its fragmentation pattern to those for other geometric isomers (Table I). In agreement with earlier work, acetophenone has two distinct ions with significant intensity in its mass spectrum: $C_6H_5^+$ (m/e = 77) and $C_6H_5CO^+$ (m/e = 105).[4,5] The product formed at 275 K has the same fragmentation pattern within experimental error. Notably, only small amounts (<1%) of the $C_6H_5CH_2^+$ ion (m/e = 91) are observed in the mass spectra of either acetophenone itself or the styrene oxidation product. On this basis, styrene oxide and phenylacetaldehyde can be excluded since the $C_6H_5CH_2^+$ ion is the most intense ion in their mass spectra. Other geometric isomers, dihydrobenzofuran, vinyl phenyl ether, and various tolualdehydes, were also excluded as products on the basis of qualitative differences between their fragmentation patterns[5] and that of the oxidation product.

Independent studies of acetophenone adsorbed on Rh(111)-p(2×2)-O suggest that the rate of evolution of gaseous acetophenone in the styrene oxidation process is limited by desorption. Acetophenone desorbs from Rh(111)-p(2×2)-O in a peak centered at 275 K with a small peak extending to 370 K. In addition, both acetophenone-d_0 and -d_8 are evolved with essentially the same kinetics during temperature-programmed reaction of styrene-d_8 in the presence of a small amount of coadsorbed acetophenone-d_0.

Temperature-programmed reaction of an equimolar mixture of styrene-d_8 and -d_0 on Rh(111)-p(2×2)-O shows that some reversible C–H(D) bond activation occurs prior to acetophenone evolution. Acetophenone-d_8, -d_7, -d_1, and -d_0 are evolved with similar kinetics in ratios of 1.0:0.3:0.4:0.8 during temperature-programmed reaction of an equimolar mixture of styrene-d_0 and -d_8. No other isotopes were observed.

The oxidation chemistry observed on the Rh(111)-p(2×2)-O surface is distinctly different from that observed for other heterogeneous systems. In related preliminary studies on Rh(111)-p(2×2)-O, propene is oxidized to acetone with kinetics and selectivity comparable to those of the styrene oxidation.[1] These data are strong evidence that allylic C–H bond activation does *not* control oxidation kinetics and selectivity on Rh(111)-p(2×2)-O, in contrast to Ag + O and metal oxide catalysts.[2,6,7] If allylic C–H bond activation controls selectivity, propene, which contains an allylic hydrogen, should be more reactive than styrene, which has none. Indeed, on Ag(110) containing adsorbed atomic oxygen, allylic C–H bonds are most reactive, resulting in the total combustion of propene, for example.[7] In contrast, norbornene[8] and styrene,[9] neither of which contain allylic protons, are selectively epoxidized by oxygen chemisorbed on Ag(110) and Ag(111), respectively.

The mechanism of alkene oxidation to ketones is likewise different for transition-metal complexes that employ molecular oxygen or peroxides as oxidants.[2,10–12] Only atomic oxygen is adsorbed on the Rh(111)-p(2×2)-O surface since the overlayer is prepared at 300 K, well above the desorption temperature of 150–200 K for O_2 adsorbed on Rh(111).[13] Furthermore, no evidence for molecular oxygen is obtained from either X-ray photoelectron or temperature programmed reaction experiments in our lab. Molecular oxygen is expected to have an O(1s) binding energy 1.2 eV higher than that of atomic oxygen,[14] and none is detected. Molecular oxygen desorbs from Rh(111) at ~150 K.

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Clearly, mechanisms that involve oxidation by O_2 or peroxides can be ruled out for Rh(111)-p(2×2)-O.

Mechanisms involving OH insertion into the C=C bond of alkenes have also been proposed for some Rh complexes.[11] We have no evidence for the presence of adsorbed OH on the Rh(111)-p(2×2)-O surface during alkene reaction. Chemisorbed OH would produce gaseous water below 250 K,[15,16] yet no water is formed below 350 K during sytrene reaction (Figure 1). Furthermore, no OH is detected in X-ray photoelectron spectra.

The oxidation of styrene to acetophenone by oxygen adsorbed on Rh(111)-p(2×2)-O is an unprecedented reaction for both homogeneous and heterogeneous systems. This study demonstrates that the acidity of C-H bonds does not control selectivity or kinetics for this oxidation reaction. Future work will be directed toward investigation of the mechanism of this unusual process.

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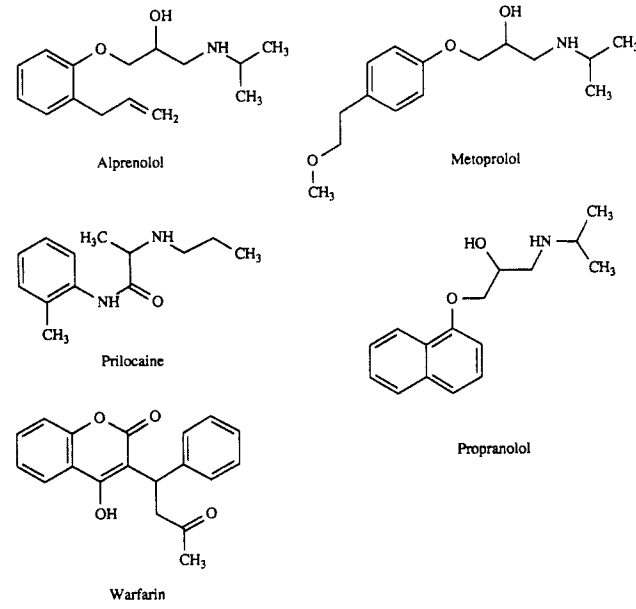

Figure 1. Structures of the solutes.

Immobilized Cellulase (CBH I) as a Chiral Stationary Phase for Direct Resolution of Enantiomers

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The growing need for analytical as well as preparative methods for separation of enantiomers in the life sciences has led to an extensive search for such methods. To the best of our knowledge, no one has reported that the easily available cellulases could be used as chiral selectors.

About 5×10^{14} kg of cellulose is converted in nature each year.[1] The most important actors in this process are fungi and bacteria, which produce the enzymes, cellulases, which catalyze the cleavage of the glycosidic bonds in the cellulose, i.e., the degradation of cellulose in nature. Fungi are efficient producers of cellulases, and as much as 20 g of different cellulases, e.g., cellobiohydrolases and endoglucanases, per liter can be isolated from the culture filtrate of the fungus *Trichoderma reesei*.[2] Cellobiohydrolase I, CBH I, is the quantitatively dominating cellulase formed by the fungi *T. reesei*,[2] *Phanerochaete chrysosporium*,[3] and *Penicillium pinophilum*,[4] and there are good reasons to believe that it is widespread among fungi that can attack crystalline cellulose. CBH I is an acidic glycoprotein with a M_W in the range 60 000–70 000 and the isoelectrical point pH 3.5–3.6, and in the case of the *Trichoderma*, both protein[5] and gene[6] are well characterized. The CBH I enzyme, like all *Trichoderma* cellulases, has a common structural organization with a short terminal binding domain (36 amino acids) connected to the main part of the protein, the core, with a flexible arm.[2] The three-dimensional structure of the binding domain has been determined by 2-D NMR.[7] The interconnecting region is rich in serine, threonine, and proline residues and is highly glycosylated. The core is catalytically active and can easily be separated from the binding domain by limited proteolysis. The core can be crystallized, and in the case of CBH II, the three-dimensional structure has been solved.[8]

Table I. Chromatographic Resolution of Racemic Drugs on Cellulase–Silica CPS[a]

	pH 4.7			pH 6.8[b]		
compd	k'_1	α	R_s	k'_1	α	R_s
alprenolol	0.16	5.1	4.8	2.8	8.3	4.9
metoprolol	0.10	1.7	0.7	0.81	2.6	3.9
prilocaine	<0.01			0.13	2.1	1.2
propranolol	0.46	2.6	4.6	6.2	4.7	4.3
warfarin[c]	3.9	1.3	1.2	0.75	1.0	

[a] Conditions are shown in Figure 2. [b] Eluent: sodium–phosphate buffer pH 6.8, $I = 0.01$, containing 0.5% 2-propanol. (+)-Norefedrin (pH 4.7) or buffer solution without 2-propanol (pH 6.8) was used as a marker for t_0, $k' = (t_R - t_0)/t_0$, $\alpha = k'_2/k'_1$, $N = 16(t_r/t_w)^2$, $R_s = (N^{1/2}k'_2(\alpha - 1))/(4(1 + k'_2)\alpha)$, where t_0 is the retention time of a nonretarded solute, k'_1 the capacity factor of the first eluted enantiomer, k'_2 the capacity factor of the last eluted enantiomer, α the selectivity factor, N the number of theoretical plates, R_s the resolution, and t_w the bandwidth at base line. [c] UV detection at 306 nm.

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