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Ketone Coupling on Reduced TiO_2 (001) Surfaces: Evidence of Pinacol Formation

Keith G. Pierce and Mark A. Barteau*

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

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Reductive coupling of acetone and acetophenone was investigated in temperature-programmed desorption (TPD) studies on both reduced (Ar^+-bombarded) and oxidized TiO_2 (001) surfaces. The principal reaction product of either ketone on the reduced surface was a symmetric olefin with twice the carbon number of the reactant. 2,3-Diphenyl-2-butene comprised over 65% of the volatile carbon-containing species desorbed from the reduced surface following acetophenone adsorption. The main side reactions which yielded products of the same carbon number as the reactants included deoxygenation to form olefins and deoxygenation plus hydrogenation to yield saturated species. The yield of reduction products was greatly diminished on the oxidized TiO_2 (001) surface; the yield of 2,3-dimethyl-2-butene, the reductive coupling product of acetone, decreased 10-fold with respect to the yield from the reduced surface. This decrease in activity for reductive coupling is similar in scale to that observed for benzaldehyde coupling on the same surfaces, supporting the conclusion that both ketone and aldehyde coupling reactions occur at ensembles of Ti cations able to undergo a four-electron oxidation. Phenyl groups adjacent to the carbonyl carbon have the greatest effect on the carbonyl coupling reaction, giving significantly higher yields of the coupled olefin product. The observation of a small amount of the pinacol, 2,3-diphenyl-2,3-butanediol, during acetophenone TPD is the first direct evidence that the carbonyl coupling reaction on reduced TiO_2 surfaces proceeds through a pinacolate intermediate, as it does for the McMurry reaction carried out in liquid−solid slurries.

Introduction

Discovered almost simultaneously by three groups over 20 years ago,[1−3] the reductive carbonyl coupling reaction to yield symmetric olefins over titanium reagents has proven to be an extremely useful tool in synthetic organic chemistry. Notable achievements utilizing this chemistry include a convenient one-step synthesis of β-carotene from retinal,[3,4] efficient synthesis of cycloalkenes with ring sizes from C_3 to C_{20},[5,6] as well as its application to a critical ring closure step in the first laboratory syntheses of taxol.[7] This reaction typically involves the reduction of $TiCl_3$ by agents such as $LiAlH_4$ or Zn−Cu in a liquid slurry, followed by exposure to the carbonyl compound which undergoes deoxygenation and coupling to form the olefin. Homogeneous complexes of titanium have also been utilized as for this reaction.[8]

Recent studies in our group have demonstrated the ability to couple a number of carbonyl compounds on reduced single-crystal TiO_2 surfaces under ultrahigh vacuum (UHV) conditions.[9−12] Detailed examination of the coupling of benzaldehyde to produce stilbene over these reduced TiO_2 surfaces[11] illustrated the effectiveness of these surfaces for the McMurry chemistry (up to 72% of the benzaldehyde reacted formed the reductive coupling product). By utilizing temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS), the active sites for stilbene formation were determined to be ensembles of reduced titanium cations (Ti^{+1}, Ti^{+2}, and Ti^{+3}) collectively able to undergo a four-electron oxidation. Previous studies of slurry-phase Ti reagents are still divided over the identity of the active site; evidence for Ti^0,[13−15] Ti^{+1},[15−18] and Ti^{+2} [1,15] exists. Our results indicate the value of techniques such as XPS to investigate the gas−solid heterogeneous reaction under UHV conditions, contributing important information concerning the nature of the active site.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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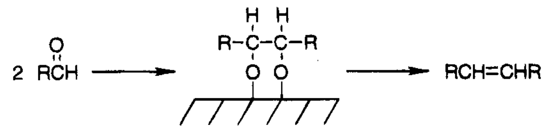
The mechanism of the McMurry reaction is believed to involve a pinacolate intermediate,[5,6] which undergoes deoxygenation to yield an olefin:



Pinacols (HOCHRCHROH) can be produced in good yield under the correct reaction conditions in the liquid phase.[19] XPS studies to identify the intermediates involved in benzaldehyde coupling to stilbene on reduced TiO_2 surfaces[11] were inconclusive; adsorbed benzaldehyde and its reaction products, including stilbene, unfortunately yield indistinguishable spectra. No pinacol products were observed during TPD experiments for any of the carbonyl compounds previously examined.[9-12] Thus, to this point, little evidence has emerged to clarify the identity of intermediates involved in reductive carbonyl coupling on reduced TiO_2 surfaces.

We investigate here the reactivity of acetone and acetophenone on reduced TiO_2 (001) surfaces to determine the effect of substituent group (aromatic and alkyl) on the yield of reductive carbonyl coupling products. As shown below, these studies have provided the first evidence for pinacol formation in gas–solid reductive carbonyl coupling by titanium oxides.

Experimental Section

The experimental methods utilized in this work have been described in detail elsewhere.[20,21] All experiments were conducted in a modified Physical Electronics Model 548 surface analysis system equipped with a UTI 100C quadrupole mass spectrometer, LEED optics, a cylindrical mirror analyzer for Auger electron spectroscopy, and a sputter ion gun. Base pressures of 10^{-10} Torr were maintained through the combined use of ion, titanium sublimation, and turbomolecular pumping.

A (001)-oriented TiO_2 rutile single-crystal sample was mechanically polished using sequentially finer grades of diamond paste, concluding with 0.25 μm. The polished crystal was mounted on a holder made of 0.127 mm tantalum foil and spot-welded to a 0.5 mm tantalum wire connected to a high-current/low-voltage power supply used for sample heating. Temperature was monitored with a chromel–alumel thermocouple attached to the crystal with zirconia-based high-temperature cement. Prior to conducting any TPD experiments, the crystal was cleaned by repeated cycles of argon ion bombardment and annealing at 950 K until no noticeable impurities, including carbon, were observed using Auger electron spectroscopy. Before each adsorption and temperature-programmed desorption experiment, the surface was bombarded using an argon ion beam (1.5 keV) at normal incidence for 1 h and was then annealed in vacuum at the desired temperature for at least 45 min. After preparation of the surface, the reagent of interest was adsorbed onto the surface to saturation coverage and the chamber pressure reduced to 2.5×10^{-10} Torr before initiating the TPD heating ramp. An IBM PC was utilized to control the temperature ramp (0.9 K/s) and mass spectrometer during each TPD run and to store experimental data. All masses up to 300 amu (the highest mass obtainable with this mass spectrometer) were checked for each reactant (in three separate TPD experiments monitoring 110 masses) and the high-resolution data presented here were obtained by monitoring fewer than 30 masses per individual TPD experiment.

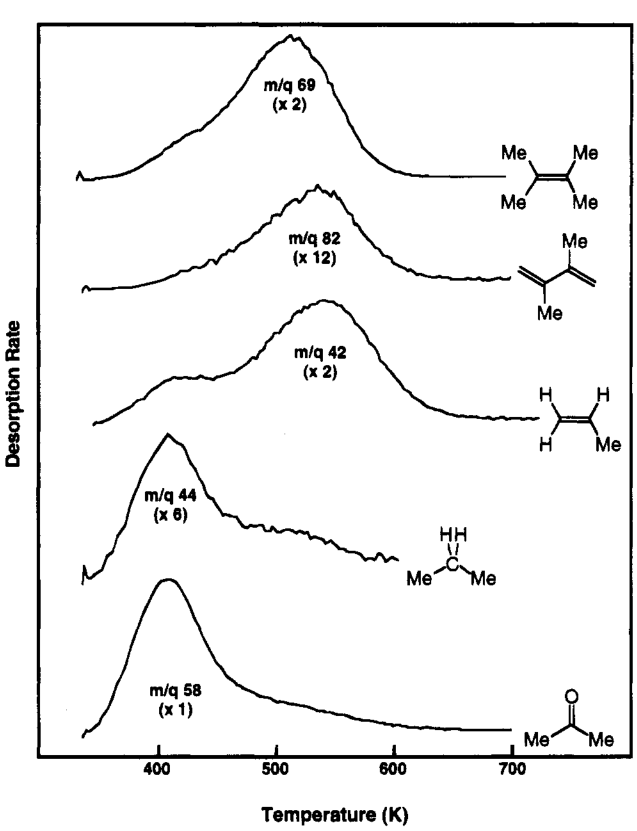


Figure 1. TPD spectra following acetone adsorption at room temperature on the ion-bombarded (300 K) TiO_2 (001) surface.

Acetone (99.9+%, Aldrich), 2,3-dimethyl-2-butene (99+%, Aldrich), acetophenone (99+%, Aldrich), styrene (99+%, Aldrich), and ethylbenzene (99+%, Aldrich) were used after purification by repeated freeze–pump–thaw cycles. Cracking patterns of pure components were recorded by introducing the reagent into the chamber at 5×10^{-9} to 1×10^{-8} Torr and recording the mass spectrometer signal vs *m/q* ratio. To aid in product identification, pure component cracking patterns of molecules previously examined were also utilized (benzene, 2,3-dimethyl-1,3-butadiene, propylene,[20] and toluene[11]).

Results

I. Acetone TPD on the Ar$^+$-Bombarded TiO_2 (001) Surface. TPD spectra of acetone adsorbed at room temperature on the ion-bombarded TiO_2 (001) surface reveal a number of reduction products, both unimolecular and bimolecular, as well as significant amounts of acetone evolving from the surface. Acetone TPD spectra on this surface are presented in Figure 1; quantitative yields of the major volatile products are furnished in Table 1. Four products of acetone reduction were observed in addition to acetone. Significant peaks at *m/q* 84, 82, 69, and 67 at 515 K and 535 K were indicative of bimolecular coupling products. The peaks at *m/q* 84 and 69 were coincident, as were the peaks at *m/q* 82 and 67, implying two distinct products with molecular weights of 84 and 82 amu, respectively, both containing pendant methyl groups. On the basis of the reduced nature of the surface (as well as the absence of peaks, e.g., at *m/q* 31, indicative of an oxygen-containing product) these products were assigned the molecular formulas C_6H_{12} and C_6H_{10}. The C_6H_{12} product, based on the ratio of the peaks at *m/q* 84 and 69, could be identified as 2,3-dimethyl-2-butene, the expected reductive carbonyl coupling product. 2,3-Dimethyl-2-butene was the predominant product

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Table 1. Product Yields for Acetone TPD on the Ion-Bombarded (300 K) TiO_2 (001) Surface

product	*m/q* ratio of principal fragment used for yield determination	peak temp (K)	fractional yield[a]
C_6H_{12} (2,3-dimethyl-2-butene)	69	515	0.261
C_6H_{10} (2,3-dimethyl-1,3-butadiene)	82	535	0.067
$CH_3CH_2CH_3$ (propane)	44	410	0.065
CH_2CHCH_3 (propylene)	42	420, 545	0.208
CH_3COCH_3 (acetone)	58	410	0.399

[a] Yields represent the fraction of the carbon content of all desorbing species contained in each species.

of the reaction of acetone on the reduced TiO_2 surface, accounting for 26% of the carbon content of desorbing species. Several examples of the coupling of carbonyl compounds (e.g., aldehydes and cyclic ketones) to yield symmetric olefins on reduced TiO_2 (001) surfaces have been demonstrated,[9-12] and the coupling of acetone to form 2,3-dimethyl-2-butene has been reported using low-valent organotitanium complexes.[8] The ratio of the peaks at *m/q* 82 to 67 for the C_6H_{10} product was consistent with that of 2,3-dimethyl-1,3-butadiene. The yield of this product was approximately one-quarter of that for 2,3-dimethyl-2-butene. 2,3-Dimethyl-1,3-butadiene is probably formed by a secondary dehydrogenation of the carbonyl coupling product 2,3-dimethyl-2-butene.

Two unimolecular reduction products of acetone were observed. Propylene (*m/q* 42) and propane (*m/q* 44) were identified after subtraction of contributions attributable to the bimolecular products and acetone. Propylene is the simplest product formed from the unimolecular deoxygenation of acetone, requiring no additional hydrogen and the net internal migration of only a single hydrogen atom, while propane requires the addition of two hydrogen atoms. Propane desorbed at the lowest temperature of any reaction product (410 K) and exhibited a significant high temperature tail extending to 580 K. Propylene desorbed in a broad state, exhibiting a major peak at 545 K and a lesser peak around 420 K. This two-state desorption was similar to that observed for propylene produced by hydrogenation of methylacetylene[20] and allene[22] on ion-bombarded TiO_2 (001) surfaces. Hydrogen necessary for the production of propane is probably generated through the total decomposition of a portion of the adsorbed acetone to oxidize the surface and yield carbon and hydrogen species. XPS studies of formaldehyde,[23] carboxylic acids,[24] and benzaldehyde[11] on reduced TiO_2 (001) surfaces have shown small amounts of residual carbon after completion of TPD experiments, indicative of the total decomposition of a fraction of the adsorbate layer. On the basis of the amount of propane observed, about 3% of the initial coverage of acetone must undergo complete decomposition to account for the hydrogen needed (after including the hydrogen generated through the production of 2,3-dimethyl-1,3-butadiene).

About 40% of the volatile carbon-containing species desorbed as the parent molecule, acetone (*m/q* 58). Acetone desorbed at 410 K with a significant high-temperature tail which disappeared by 650 K. Of the volatile reaction products, the two major species were 2,3-dimethyl-2-butene and propylene, with selectivities (defined as the fraction of carbon converted contained in each product) of 43% and 35%, respectively. 2,3-Dimethyl-1,3-butadiene and propane were produced in approximately equal, but smaller, amounts (with selectivities of 11% each).

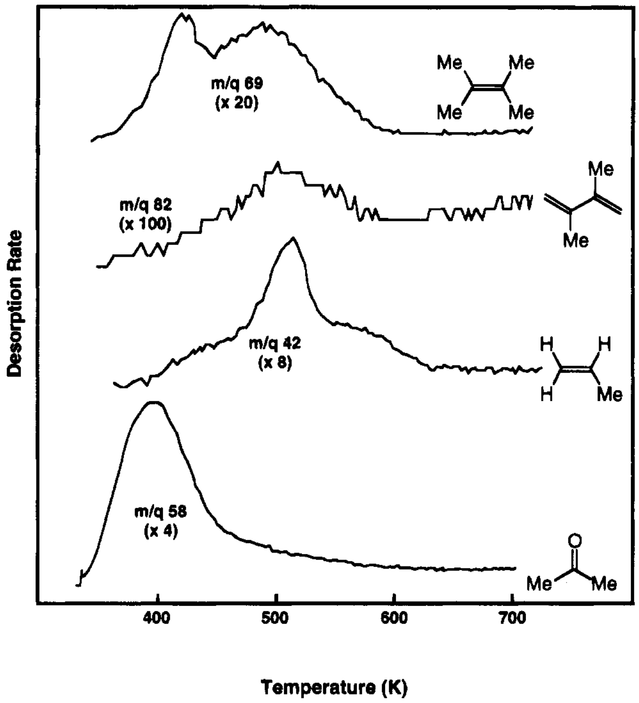

Figure 2. TPD spectra following acetone adsorption at room temperature on the 850 K-annealed TiO_2 (001) surface.

II. Acetone TPD on the 850 K-Annealed TiO_2 (001) Surface. Annealing the surface to 850 K prior to acetone exposure oxidized the surface completely (only Ti(4+) cations were detectable by XPS[23-25]) and sharply decreased formation of reduction products. TPD spectra of acetone on the 850 K-annealed, fully-oxidized TiO_2 (001) surface are presented in Figure 2, with the quantitative product yields in Table 2 (Note: The fractional product yields on the 850 K-annealed surface listed in Table 2 are also shown normalized with respect to those from the ion-bombarded surface (Table 1) to facilitate comparison of the activities of these two surfaces. The multiplication factors associated with each TPD trace in Figure 2 are on the same scale as those in Figure 1.) All products observed on the reduced surface (except propane) were observed on the 850 K-annealed surface, but in drastically reduced amounts. The total quantity of volatile species desorbed from the 850 K surface, including unreacted acetone, was only 17% of that observed on the reduced surface. The major reductive coupling product (2,3-dimethyl-2-butene) desorbed in two distinct states at 420 and 490 K, but with a total yield only 10% of that observed on the reduced surface. The other bimolecular coupling product, 2,3-dimethyl-1,3-butadi-

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Table 2. Product Yields for Acetone TPD on the 850 K-Annealed TiO_2 (001) Surface

product	m/q ratio of principal fragment used for yield determination	peak temp (K)	fractional yield[a]	normalized yield[b]
C_6H_{12} (2,3-dimethyl-2-butene)	69	420, 490	0.161	0.027
C_6H_{10} (2,3-dimethyl-1,3-butadiene)	82	500	0.026	0.004
CH_2CHCH_3 (propylene)	42	510	0.205	0.034
CH_3COCH_3 (acetone)	58	395	0.608	0.101

[a] Fractional yield represents the fraction of the carbon content of all desorbing species contained in each species. [b] Normalized yield is based on the ion-bombarded surface acetone TPD (Table 1).

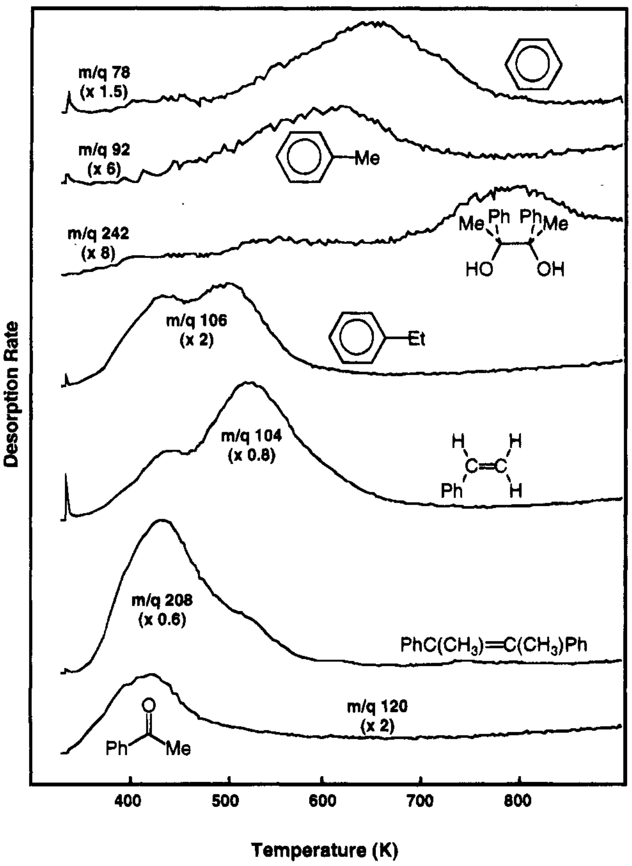

Figure 3. TPD spectra following acetophenone adsorption at room temperature on the ion-bombarded (300 K) TiO_2 (001) surface.

ene, desorbed in a broad peak at 500 K in barely detectable amounts (only 6% of that observed on the reduced surface). Propylene desorbed in a sharp peak at 510 K superimposed on a broader state centered at approximately the same temperature. The production of propylene on the 850 K surface was 16% of that on the reduced surface. Acetone desorbed in a low-temperature peak at 395 K similar to that observed on the reduced surface, but with slightly lower temperature (395 vs 410 K) and smaller amounts (about one-fourth of that on the reduced surface).

III. Acetophenone TPD on the Ar^+-Bombarded TiO_2 (001) Surface. Acetophenone TPD on the reduced TiO_2 (001) surface exhibited a larger assortment of reductive products than acetone on the same surface, as well as greater conversion of the parent molecule. TPD spectra of acetophenone adsorbed at room temperature on the Ar^+-bombarded TiO_2 (001) surface are presented in Figure 3, with fractional yields of the volatile products shown in Table 3. Significant peaks observed at m/q 193, 208, and 242 provided clear evidence of coupling. Two distinct states could be identified; one major product with contributions at m/q 193 and 208 desorbing at 430 K and exhibiting a high-temperature shoulder at 510 K, and one minor product characterized by a peak at m/q 242 at high temperatures (a broad peak around 785 K). The product at 430 K could readily be assigned to the expected reductive coupling product, 2,3-diphenyl-2-butene. 2,3-Diphenyl-2-butene was by far the dominant product observed during TPD of acetophenone from reduced TiO_2 (001) surfaces, accounting for 65% (total carbon-content basis) of the volatile species observed. This high yield of the reductive coupling product is consistent with that observed during benzaldehyde coupling to form stilbene on this reduced surface (56%),[11] as is the observed peak temperature (440 K for stilbene vs 430 K for 2,3-diphenyl-2-butene).

Whereas the production of 2,3-diphenyl-2-butene was anticipated on the basis of the results of acetone TPD on this surface, assignment of the high-temperature product at m/q 242 was more difficult. This product desorbed at a significantly higher temperature than any other product observed in other studies of carbonyl compounds on these reduced surfaces (as noted above, the highest temperature product from acetone desorbs below 550 K). The highest molecular weight product observed from other carbonyl compounds on the reduced TiO_2 (001) surface was the olefinic reductive coupling product; for example, stilbene (180 amu) was the largest product observed from benzaldehyde (106 amu)[9,11] and, as shown above, 2,3-dimethyl-2-butene (84 amu) was the largest product of acetone (m/q 58). If one assumes that the peak at m/q 242 is indicative of the parent mass of the product, the high-temperature product would have a molecular weight 34 amu greater than 2,3-dimethyl-2-butene (208 amu). The most plausible product having a molecular weight of 242 amu consistent with the reductive chemistry observed on these surfaces is 2,3-diphenyl-2,3-butanediol. This is the expected pinacol product of acetophenone, and pinacolates are widely thought to be intermediates in the McMurry coupling reaction.[5,6] It has been repeatedly demonstrated that pinacol products can be isolated in high yield through the interaction of carbonyl compounds with reduced Ti species (such as $TiCl_3/LiAlH_4$), and then converted to olefins by exposure to more reduced Ti.[5,6] It is therefore not surprising that small amounts of a pinacol product would be observed in the reductive coupling of acetophenone on reduced TiO_2 (001) surfaces. What is surprising is that no other carbonyl compound examined on this surface to date has produced a pinacol product, although a number of different compounds have been examined and such products have been searched for.[9-12,26] However, other experiments have provided evidence for the existence of pinacolate intermediates on reduced TiO_2 (001) surfaces during these coupling reactions. XPS C(1s) spectra of adsorbed cyclic ketones on the reduced TiO_2 (001) surface

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Table 3. Product Yields for Acetophenone TPD on the Ion-Bombarded (300 K) TiO_2 (001) Surface

product	*m*/*q* ratio of principal fragment used for yield determination	peak temp (K)	fractional yield[a]
$C_6H_5COCH_3$ (acetophenone)	120	415	0.058
$C_6H_5CH_2CH_3$ (ethylbenzene)	106	435, 495	0.084
$C_6H_5CHCH_2$ (styrene)	104	435, 520	0.157
$C_6H_5CH_3$ (toluene)	92	600	0.010
C_6H_6 (benzene)	78	645	0.023
$C_{16}H_{16}$ (2,3-diphenyl-2-butene)	208	430	0.651
$C_{16}H_{18}O_2$ (2,3-diphenyl-2,3-butanediol)	242	785	0.016

[a] Yields represent the fraction of the carbon content of all desorbing species contained in each species.

have shown evidence of small amounts of alkoxide species, consistent with pinacolate intermediates.[10] Similar XPS studies of benzaldehyde could not eliminate the possibility of small amounts of surface pinacolates.[11] Production of large amounts of ethylene during TPD of ethylene glycol on reduced TiO_2 (001) surfaces is indicative of the ability of these surfaces to produce olefins from pinacols.[27] The high temperature of the desorption peak for the pinacol product can be explained as follows. Previous XPS results demonstrated that the deoxygenation step of the coupling reaction occurred virtually to completion upon adsorption of the carbonyl compound onto a reduced surface.[10] Our results imply that upon adsorption, a small portion of the acetophenone is not completely converted and forms an intermediate surface pinacolate species. This species remains on the surface until at higher temperatures a sufficient supply of hydrogen formed from other reactions (e.g., carbon deposition) recombines with these pinacolates, forming the observed volatile pinacols.

Four unimolecular reduction products of acetophenone were produced. Analogous to the production of propylene and propane from acetone, styrene (*m*/*q* 104), and ethylbenzene (*m*/*q* 106) were observed. Both desorbed in two peaks; styrene in a major peak at 520 K and a minor one at 435 K, and ethylbenzene in two peaks of similar size at 435 and 495 K. As was observed previously, the more hydrogenated product was produced in lesser quantities (about half as much ethylbenzene as styrene). Significantly smaller amounts of two other products, benzene (*m*/*q* 78) and toluene (*m*/*q* 92), were produced. Both of these products desorbed in very broad states; toluene at 600 K and benzene at 645 K. Toluene and benzene production require not only oxygen abstraction from acetophenone, but carbon−carbon bond scission as well.

Small amounts of acetophenone desorbed at 415 K. On the basis of the amount of volatile products observed, over 94% of the acetophenone adsorbed was converted to other products on the reduced TiO_2 (001) surface. As mentioned above, 2,3-diphenyl-2-butene was by far the largest product, with a selectivity of nearly 70%. The major unimolecular products were styrene and ethylbenzene, accounting for 16% and 8% of the volatile products desorbed, respectively. The remaining three products were produced in small amounts, none exceeding 3% of the initial acetophenone coverage.

Discussion

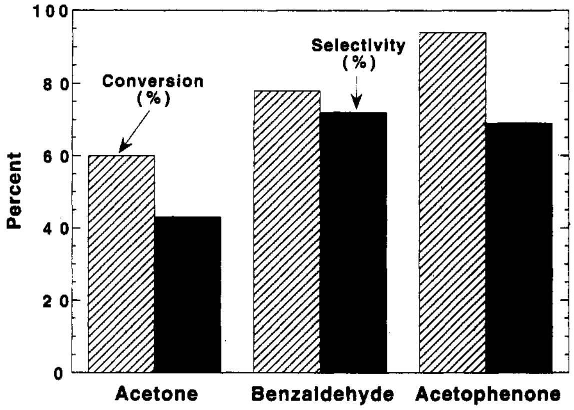

Figure 4. Conversion (percent) of the ketone and selectivity (percent) for production of the carbonyl coupling product for acetone, benzaldehyde,[11] and acetophenone.

Both unimolecular and bimolecular reduction products result from the interaction of ketones with the Ar^+-bombarded TiO_2 (001) surface. Two major unimolecular products are typically observed: unsaturated hydrocarbons produced by the simple deoxygenation of the ketone, and saturated hydrocarbons produced by deoxygenation and hydrogenation. The principal bimolecular product (indeed, the predominant product overall) from all reactants examined was the symmetric olefin produced by reductive carbonyl coupling. The effectiveness of reduced TiO_2 surfaces for McMurry coupling chemistry is remarkable, especially given the UHV conditions of these experiments. For acetophenone, over 65% of the volatile carbon was contained in this product.

Through comparison of the yields of the reductive coupling products of acetone and acetophenone with those observed previously for benzaldehyde,[9,11] the effects of substituent groups on the efficacy of the carbonyl coupling chemistry on reduced TiO_2 surfaces can be determined. Comparisons of conversion and selectivity to the respective carbonyl coupling products for acetone, benzaldehyde, and acetophenone are presented in Figure 4. Acetone clearly exhibits significantly lower conversions and reductive coupling product selectivities than benzaldehyde or acetophenone. The difference between benzaldehyde and acetophenone is smaller, with acetophenone showing higher conversions but similar selectivity to benzaldehyde for bimolecular coupling. From this comparison, the greatest enhancement of reductive coupling activity is observed when an aromatic substituent group is present vs an alkyl (methyl) group. Kahn and Rieke[28] and McMurry[5] have shown that aromatic ketones are easier to couple than aliphatic ones and in general give higher yields for the coupling product in liquid−solid slurries. However, direct comparisons of yields, effects of substituent groups, etc., between our work and liquid-phase slurry studies can be problematic. When studying

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the McMurry coupling of compounds in liquid–solid slurries of reduced titanium species, the efficiency of the coupling reaction, as measured by an overall yield, results from repeated encounters of the carbonyl compound with reduced titanium centers. Compounds adsorbed on the active titanium surface can either react or desorb intact; those that desorb intact, however, can adsorb again on another site and react. Because of this inherent "recycle" effect encountered in solution-phase chemistry, even if aromatic ketones are more likely to generate reductive coupling products, as long as other products are not generated (e.g., unimolecular reduction products), the overall yield of aliphatic and aromatic ketones can be substantially the same, or at least not representative of the true differences in reactivity of the molecules in question, especially for experiments with long reaction times and high conversions. In our studies on single-crystal TiO_2 surfaces using TPD experiments, because of the low pressures involved, readsorption is essentially eliminated, and coupling efficiencies for a single interaction of each molecule with the surface are generated. These studies give a unique insight into the true efficiency of the active surface that is otherwise virtually impossible to determine. Additionally, if one recognizes that our experiments are representative of only one turnover of the reduced TiO_2 surfaces, the high yield of the McMurry coupling product is all the more surprising.

Two results from this examination of ketone reactivity on TiO_2 (001) surfaces help to expand and clarify our understanding of the active site and mechanism involved in the carbonyl coupling reaction on these surfaces. In previous work on reduced TiO_2 (001) surfaces, it was shown that reductive coupling activity tracks the extent of reduction of surface Ti cations below the +4 state. This implies that the active site for carbonyl coupling of benzaldehyde can be any ensemble of reduced Ti cations (+1, +2, and +3) able to undergo a four-electron oxidation.[9,11] As we have shown, significant amounts of the olefin product of reductive coupling are produced from acetone and acetophenone on the Ar^+-bombarded surface, as was observed for benzaldehyde;[9,11] in fact, as seen in Figure 4, benzaldehyde and acetophenone are quantitatively similar in conversion and selectivity for the olefin product on these surfaces. For acetone, the decrease in yield of the reductive carbonyl coupling product 2,3-dimethyl-2-butene from the Ar^+-bombarded to the 850 K-annealed surface is comparable to that observed for the production of stilbene from benzaldehyde on similar surfaces;[9,11] both exhibit approximately an order of magnitude decrease (9.7 for 2,3-dimethyl-2-butene and 8.3 for stilbene). From this evidence it appears, not surprisingly, that ketones and aldehydes share a common active site for carbonyl coupling on reduced TiO_2 surfaces. On the basis of the production of 2,3-diphenyl-2,3-butanediol during acetophenone TPD, however, we now have important evidence concerning the mechanism of the carbonyl coupling reaction on reduced TiO_2 surfaces. The vast majority of previous liquid-phase work with titanium reagents has implicated a pinacolate intermediate in the carbonyl coupling reaction;[5,6] however, initial studies on single-crystal TiO_2 surfaces with benzaldehyde showed no evidence of a volatile pinacol product.[9,11] The identification of a small amount of the expected pinacol product during acetophenone TPD provides evidence that the mechanism of gas–solid carbonyl coupling on reduced TiO_2 surfaces proceeds through the same pinacolate intermediate that is commonly observed for the heterogeneous slurry-phase reaction.

Conclusions

Ar^+-bombarded, reduced TiO_2 (001) surfaces reductively couple ketones to form symmetric olefins in significant amounts; 2,3-diphenyl-2-butene is produced from acetophenone with a selectivity of almost 70%. The respective bimolecular McMurry coupling products are the principal result of both acetone and acetophenone reactions on this surface. The major unimolecular reduction reaction involves deoxygenation of the ketone to form an olefin (propylene from acetone, styrene from acetophenone); smaller amounts of a unimolecular hydrogenation product were also observed (propane from acetone, ethylbenzene from acetophenone). On the basis of this work and previous work with benzaldehyde on reduced TiO_2 surfaces, pendant phenyl groups adjacent to the carbonyl group enhance both the conversion of the aldehyde or ketone and the selectivity to the reductive coupling product. The yield of all reduction products, as well as the reactant uptake, decreased drastically for acetone on a fully-oxidized TiO_2 (001) surface (compared to the reduced surface); the yield of the reductive carbonyl coupling product 2,3-dimethyl-2-butene decreased by an order of magnitude between the two surfaces, exhibiting similar yield behavior to that observed for benzaldehyde. Small amounts of 2,3-diphenyl-2,3-butanediol produced during acetophenone TPD provide the first chemical evidence for pinacol formation on reduced TiO_2 (001) surfaces, supporting the existence of pinacolate intermediates during reductive coupling to form olefins.

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