compound was prepared as described for IIIa by starting from *trans*-[$(PPh_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)Cl]BF_4$ (482 mg, 0.49 mmol), NaCl (144 mg, 2.47 mmol), and oxirane (4 mL) in 2-chloroethanol (5 mL). After it was stirred for 3 days at room temperature, the reaction mixture was evaporated to dryness, dissolved in CH_2Cl_2 (10 mL), and filtered. The filtrate was treated with Et_2O (50 mL) to give a white precipitate of the product, which was filtered and dried under vacuum: yield 233 mg (47%); mp 229–232 °C. Anal. Calcd for $C_{46}H_{41}NO_2ClP_2BF_4Pt$: C, 51.13; H, 3.92; N, 1.26. Found: C, 51.48; H, 3.86; N, 1.22.

***cis*-$Cl_2(p\text{-}MeOC_6H_4NC)Pt[\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2O}]$ (IIIc).** This compound was prepared as described for IIIa by starting from *cis*-$Cl_2Pt(CNC_6H_4\text{-}p\text{-}OMe)_2$ (251 mg, 0.47 mmol), NaCl (81 mg, 1.41 mmol), and oxirane (4 mL) in 2-chloroethanol (5 mL): yield 63 mg (23%); mp 179–182 °C dec. Anal. Calcd for $C_{18}H_{18}N_2Cl_2O_3Pt$: C, 37.51; H, 3.14; N, 4.86. Found: C, 37.04; H, 3.10; N, 4.80.

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Registry No. **1**, 115268-38-7; **2**, 38883-39-5; **3**, 115226-76-1; **4**, 115226-77-2; **5**, 115226-78-3; **6**, 111140-04-6; **7**, 34710-33-3; **8**, 29827-46-1; **9**, 40927-13-7; **10**, 40927-16-0; **11**, 76376-35-7; **12**, 27902-71-2; Ia, 115226-79-4; Ib, 115244-43-4; Ic, 115226-80-7; Id, 115226-81-8; Ie, 115226-82-9; If, 115226-83-0; Ig, 115226-84-1; Ih, 115226-85-2; IIa, 115226-86-3; IIb, 115226-87-4; IIc, 115226-88-5; IIIa, 115244-44-5; IIIb, 115244-46-7; IIIc, 115226-89-6; *trans*-[$(PPh_3)_2Pt(CNC_6H_4\text{-}p\text{-}OMe)]BF_4$, 110313-73-0; aziridine, 151-56-4; thiirane, 420-12-2; oxirane, 75-21-8.

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Photoassisted Catalysis of the 1-Pentene Isomerization by $Fe(CO)_5$ Physisorbed onto Porous Vycor Glass

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UV photolysis of $Fe(CO)_5$ physisorbed onto porous Vycor glass under a 1-pentene atmosphere leads to quantitative formation of $Fe(CO)_4$(1-pentene). Continued photolysis leads to an active, catalytic intermediate capable of promoting alkene isomerization. Diffuse-reflectance FTIR spectra reveal intermediates that closely resemble those found in low-temperature hydrocarbon matrices. Although the spectral similarities and isomerization quantum yield, 152 ± 23, indicate a thermally activated ground-state catalyst, the cis/trans product ratio varies with irradiation time and differs from the expected thermodynamic ratio.

Introduction

Catalytic activity of iron carbonyls requires vacant or labile coordination site(s) where the substrate(s) can bind and undergo chemical transformation.[1-3] In the isomerization of olefins, for example, current data suggest $Fe(CO)_3$ as a key intermediate. Mechanistic studies performed by Grevels, Fleckner, and Hess implicate $Fe(CO)_3$ as the recurring catalytic intermediate in the thermally activated isomerization of 1-pentene.[4] Similar results occur in the photoactivated isomerization of 1-pentene, although the identity of the actual catalytic intermediate remains somewhat controversial. Chase and Weigert assign a band at 1969 cm^{-1} to active intermediate generated during photolysis of $Fe(CO)_5$ in neat 1-pentene.[5] Grant and co-workers identify $Fe(CO)_3(C_5H_{10})$ (C_3H_{10} = pentene) as the phenomenological catalyst and suggest that the catalyst lifetime, 0.2 s in neat 1-pentene, is determined by olefin dissociation, which yields a fragment that rapidly degrades to an inactive form.[6] Wrighton and co-workers propose the involvement of $Fe(CO)_3(1\text{-}C_5H_{10})_2$[7,8] and, on the basis of photolyses in low-temperature hydrocarbon matrices, suggest that the π-allyl complex $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ is potentially the essential intermediate in the catalytic cycle.[9,10] In spite of the uncertainty with respect to the molecularity of the alkene, quantum yields of isomerization in excess of unity suggest that, although the compound is generated photochemically, the actual isomerization of the alkene is accomplished by a thermally activated ground-state species.[7-10]

Recent studies have focused on the catalytic activity of hybrid systems where the precursor, $Fe(CO)_5$ or a substituted analogue, is on a support. Wrighton and co-workers have used the photocatalyzed isomerization of 1-pentene to examine the activity of iron carbonyl anchored to a styrene microporous resin.[11] UV photolysis of the surface-confined species, principally $Fe(CO)_4L$ and $Fe(CO)_3L_2$ where L designates the triarylphosphine anchor, results in CO loss and formation of a catalytic intermediate capable of effecting a number of isomerizations.[11] The cis/trans ratio obtained with the hybrid system, relative to that obtained with the analogues $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(PPh_3)_2$ in homogeneous solution, suggests controlling product distribution by surface modification.[11] Similar results are described by Suib and co-workers for the photocatalyzed isomerization of 1-pentene by $Fe(CO)_5$ adsorbed onto the outer surfaces of small-pore zeolites and in the supercages of large-pore zeolites.[12] Although decomposition of the precursor complex to either an oxidized species and/or a cluster clouds the mechanistic interpretation, this hybrid system alters both the percent conversion and the product ratio,[12] relative to those for the photoactivated isomerization in homogeneous solution.

The development of hybrid systems, particularly an understanding of their differences from homogeneous systems, rests on the characterization of the surface-confined species. Experiments in this laboratory have shown that UV photolysis of $Fe(CO)_5$ physisorbed onto Corning's Code 7930 porous Vycor glass (PVG)

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results in the efficient, stepwise formation of $Fe(CO)_n$ ($n \leq 4$) on the glass.[13] Although some of these intermediates offer the potential of catalytic activity, the material obtained after excitation of an organometallic on a nonfunctionalized oxide support does not necessarily possess a direct analogue among homogeneous catalysts. The tetracarbonyl, for example, undergoes immediate oxidative addition to form $H-Fe(CO)_4-OSi$ and $H-Fe(CO)_4-OH$, while more highly unsaturated intermediates, specifically $Fe(CO)_3$(ads) (ads designates an adsorbed species), rapidly form di- and trimeric complexes on the glass surface.[13] To probe the activity of these intermediates, we have examined the $Fe(CO)_5$(ads)–PVG system under 1-pentene. In the presence of the alkene, 350-nm photolysis of $Fe(CO)_5$(ads) leads to quantitative formation of $Fe(CO)_4(1\text{-}C_5H_{10})$(ads), which is then photochemically converted to catalytic intermediate(s). Although the quantum yield of alkene isomerization indicates a thermally activated ground-state catalyst, the cis/trans isomer ratio varies with irradiation time. Diffuse-reflectance FTIR (DRIFT) spectra reveal intermediates that spectrally resemble those found in low-temperature matrices.

Experimental Section

Materials. $Fe(CO)_5$ (Pressure Chemical Co.) was vacuum-distilled and stored in a freezer under an inert atmosphere. UV–visible and IR spectra of the distilled complex were in excellent agreement with published spectra.[14-17] $Fe_3(CO)_{12}$ (Pressure Chemical Co.) and 1-pentene (Fluka) were used as received since their electronic and IR spectra agreed with published spectra.[18-21] Spectral grade solvents were distilled over CaH_2 and stored over molecular sieves prior to use.

Code 7930 porous Vycor glass containing 70 ± 21 Å diameter cavities was obtained from the Corning Glass Works. Pieces of PVG (25 mm × 19 mm × 4 mm) and powdered PVG (325 mesh, ≤45 μm) were extracted and calcined according to previously described procedures.[13,22,23] The pieces were stored at 550 °C until needed, at which point a sample was transferred to a 4 cm × 2.2 cm × 1 cm rectangular quartz cell with a 7.62-cm O-ring joint. Teflon mounts held the sample upright, and a Pyrex top with a 2 mm high vacuum valve was attached. The cell was attached to a previously described vacuum line[13] and cooled to room temperature (22 ± 1 °C) under vacuum ($p \leq 10^{-4}$ Torr). After calcination, the powder was transferred while hot to tighly capped vials, which were stored in an oxygen- and water-free glovebox.

Impregnation Procedures. Regardless of the procedure used, all samples were impregnated with $Fe(CO)_5$ degassed by three freeze–pump–thaw cycles. Initially, impregnation with $Fe(CO)_5$ was by vapor deposition techniques where the number of moles of $Fe(CO)_5$ adsorbed was determined by differential pressure measurements.[13] Samples prepared in this manner were then used to construct a plot of $Fe(CO)_5$(ads) optical density at 350 and 400 nm vs the moles of complex adsorbed per gram of PVG. The moles of complex adsorbed onto subsequent samples, which ranged from 10^{-7} to 10^{-4} mol/g of PVG, were determined from this plot and the complex optical densities.[13] Impregnation with $Fe_3(CO)_{12}$ was accomplished by solution adsorption techniques. The absorbance of the solution phase was monitored during adsorption, and the moles of complex adsorbed was calculated from the absorbance change at 605 nm.[13] The solvent, *n*-hexane, incorporated during impregnation was removed under vacuum.

For diffuse-reflectance FTIR (DRIFT) experiments, the calcined, 325 mesh PVG powder was loaded into a previously described microreactor in a dry, inert-atmosphere box.[13] The powdered PVG was impregnated with $Fe(CO)_5$ by expanding a set quantity, generally 5 Torr in 102 mL, into the microreactor cell. After equilibration, the moles of complex adsorbed, typically 3×10^{-4} mol/g of PVG, was determined by differential pressure measurements. The vacuum manifold was then reevacuated, 1-pentene degassed by three freeze–pump–thaw cycles was admitted into the microreactor, and the desired equilibrium pressure was established.

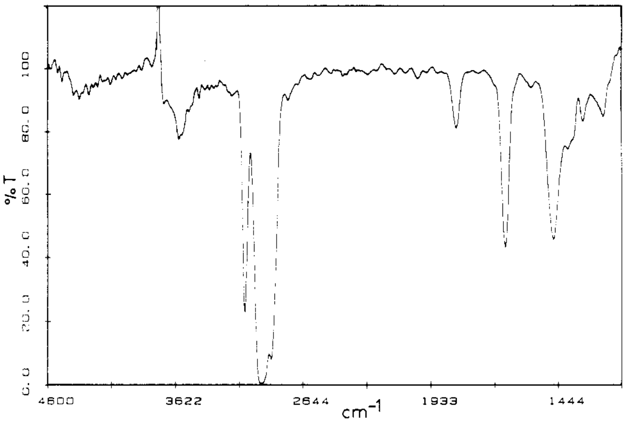

Figure 1. DRIFT spectrum of 1-pentene (160 Torr) adsorbed onto calcined PVG.

Photolysis Procedures. Impregnated samples of PVG either in vacuo or under 100 or 160 Torr of 1-pentene were irradiated in a Rayonet photochemical reactor (Southern New England Ultraviolet Co.) equipped with 350-, 310-, or 254-nm bulbs. Quantum yield measurements were limited to 350-nm excitation since competitive absorption by the glass (50% transmittance (T) at 295 nm vs air) at this wavelength is negligible. The excitation intensity at this wavelength, typically 2×10^{-9} einstein/(s cm^2), was determined by ferrioxalate actinometry.[13] Samples under 1-pentene were irradiated in a cell equipped with a gastight rubber septum. The surrounding gas phase was sampled periodically and quantitated by GC chromatography.

In the DRIFT experiments, impregnated samples in the microreactor were irradiated with 350-nm light from a Kr ion laser (Coherent Model CR3000K) or with 355-nm light from a Q-switched Nd:YAG laser (Quanta Ray Model DCR-2). The Kr laser provided 500 mW to an area, 0.13 cm^2, slightly larger than the FTIR sampling area. The exposure time was controlled with an electronic shutter (Newport Research Model 880) timed to open between the FTIR spectrometer data acquisition periods. The Nd:YAG laser provided 50 mJ (40 mW/cm^2) of 355-nm radiation to the same sample area. The laser flash lamps were synchronized with the spectrometer data acquisition rate, and the Q-switch fired between the spectrometer scans. The interferograms were treated as previously described.[13]

Physical Measurements. The surrounding gas phase was sampled periodically with a 25 μL gastight syringe (Hamilton) and analyzed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. Olefin separation was achieved with a 2 m × 3.18 mm stainless steel column packed with 80/100 Carbopack c/o 19% picric acid (Supelco). The column was maintained at 50 °C, and N_2 (20 mL/min) was used as the carrier gas. The detector temperature was 130 °C, and its response was calibrated with aliquots syringed from the photolysis cell filled with known pressures of 1-pentene. UV–visible spectra were recorded on a Cary 14 spectrophotometer adapted to hold the rectangular cells. All spectra were recorded relative to a calcined, unimpregnated sample of PVG in the reference compartment. Infrared spectra of solutions and mulls were recorded on a Perkin-Elmer Model 1330 spectrophotometer equipped with a Model 1660 data station and calibrated with polystyrene. DRIFT spectra were recorded on a Nicolet Model 60SX FTIR instrument equipped with a narrow-band MCT detector, and a Harrick's Model DRA-PMN diffuse-reflectance beam condenser adapted to hold the previously described microreactor.[13]

Results and Discussion

Adsorption. Regardless of the moles adsorbed, $Fe(CO)_5$ penetrates no more than 0.4 ± 0.1 mm into the glass. With 25 mm × 19 mm × 4 mm samples containing $\leq 10^{-7}$ to 10^{-4} mol of $Fe(CO)_5$(ads)/g of PVG, adsorption is limited to the outer volumes of glass, while the interior, ca. 80% of the total volume, remains vacant. Since the same distribution is found with other adsorbates that differ from $Fe(CO)_5$ in both size and mechanism of adsorption, the apparent penetration is taken as a measure of the deviation from surface planarity rather than population of interior

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cavities.[22-25] It was not possible to determine the distribution of the complex in the powdered glass. The more rapid rate of desorption, however, suggests that adsorption is again limited to the outer surfaces, where the larger amount adsorbed, 3×10^{-4} mol/g of PVG, reflects the larger outer surface area of the powder.[13] With both forms of the glass, the complex is on the outer surface, and its reactions are not biased by a slow mass transport of the alkene into interior portions of the glass.

Both $Fe(CO)_5$ and 1-pentene physisorb onto PVG without chemical change. The DRIFT spectrum of adsorbed 1-pentene (Figure 1) is equivalent to its fluid-solution spectrum.[21] The electronic spectrum of $Fe(CO)_5$(ads) also resembles its fluid-solution spectrum except that the lower energy ligand field transition, which appears as a 285-nm shoulder in the fluid-solution spectrum,[14,15] appears as an unresolved tail.[13] The DRIFT spectrum of $Fe(CO)_5$(ads) shows intense bands at 2004 and 2026 cm^{-1} and a weak band at 2114 cm^{-1}. Relative to the vapor- and solution-phase spectra of $Fe(CO)_5$, the bands are red shifted by ca. 8 cm^{-1}, and their relative intensities are inverted.[13] The weak band at 2114 cm^{-1}, which is assigned to the symmetric v_1 mode,[13,26] suggests that adsorption reduces the molecular symmetry from D_{3h} to C_{2v}.[27] Nevertheless, the similarity of the electronic and DRIFT spectra with the vapor- and solution-phase spectra, as well as the ability to desorb the intact complex, establish that $Fe(CO)_5$ physisorbs onto PVG without disruption of its primary coordination sphere.

Photocatalyzed Isomerization. Exposing PVG to 160 Torr of 1-pentene results in the appearance of strong absorptions in the C—H and C═C regions (Figure 1) and a corresponding decline in intensity at 3744 cm^{-1}. Evacuation of the cell reverses the spectral change; i.e., the loss of the alkene bands occurs with a proportional reappearance of the 3744-cm^{-1} Si-OH band. Although the spectral changes indicate that the alkene adsorbs onto the silanol group, there is no indication that adsorption predisposes the alkene to isomerization. GC analysis after storage of 160 Torr (3.55×10^{-4} mol) of 1-pentene over calcined PVG at 22 ± 1 °C for several hours indicates $\leq 1\%$ conversion to *cis*- or *trans*-2-pentene. Similar results occur after a 30-min, 350-nm photolysis under 160 Torr of 1-pentene; GC analysis shows no detectable ($\leq 1\%$) amounts of the isomers.

With samples containing $Fe(CO)_5$(ads), however, both thermal and photoactivated catalysis occur. Exposing PVG containing 1.8×10^{-5} mol of $Fe(CO)_5$(ads)/g of PVG to 100 Torr (2.22×10^{-4} mol) of 1-pentene results in an immediate coadsorption of $(1.0 \pm 0.2) \times 10^{-4}$ mol of alkene/g of PVG. The surface coverage by $Fe(CO)_5$(ads) is calculated to be 17%,[28] while that in the powdered glass, where the loading is 3×10^{-4} mol/g of PVG, is 45%.[28] With either sample, however, coadsorption occurs without affecting either the electronic or the DRIFT spectrum of $Fe(CO)_5$(ads). The spectral changes, which are equivalent to Figure 1, indicate that the alkene adsorbs onto silanol groups without affecting the adsorbed complex. Nevertheless, GC analysis of the surrounding vapor after storage in the dark reveals both *cis*- and *trans*-2-pentene. At 22 ± 1 °C, however, the rate of thermal catalysis, $(1.1 \pm 0.1) \times 10^{-5}$ mol/h, is negligible in comparison to the photoactivated process.

A 350-nm photolysis of a sample containing 1.8×10^{-5} mol of $Fe(CO)_5$(ads)/g of PVG under 100 Torr (2.22×10^{-4} mol) of 1-pentene results in an immediate uptake of 1-pentene (Figure 2). The initial light yellow color of the sample darkens immediately, and UV–visible spectra show a corresponding increase in absorbance in the 350–360-nm region. The increase in absorbance occurs during the induction period (Figure 2) and correlates with the initial uptake of 1-pentene. No further change occurs during isomerization. Instead, there is a nondescript broadening in the 360–400-nm region.

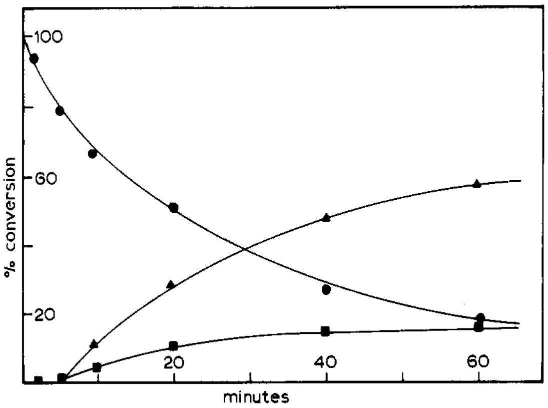

Figure 2. Plot of 1-pentene disappearance (●) and *cis*- (■) and *trans*-2-pentene (▲) formation during 350-nm photolysis of 1.86×10^{-5} mol of $Fe(CO)_5$(ads)/g of PVG under 160 Torr of 1-pentene.

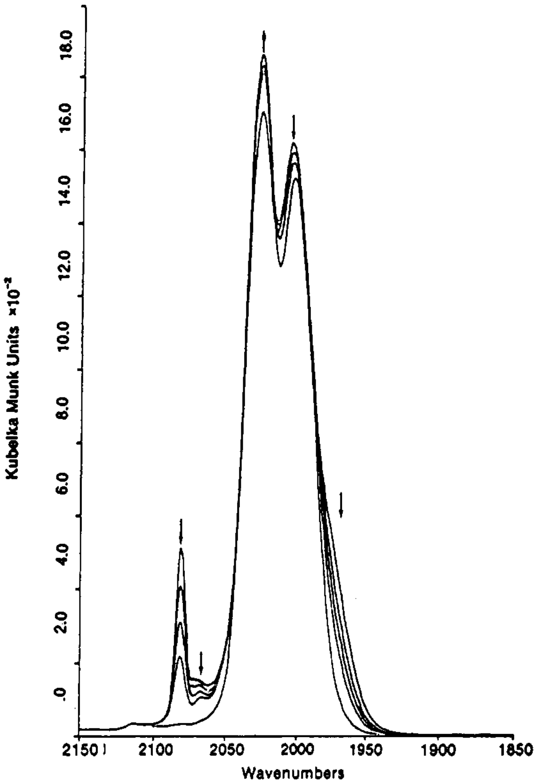

Figure 3. DRIFT spectra of $Fe(CO)_5$(ads), 3×10^{-4} mol/g of PVG, under 100 Torr of 1-pentene before and 0, 20, 60, and 100 s after a 0.4-s, 350-nm irradiation. Arrows indicate the change in intensity after photolysis.

Diffuse-Reflectance FTIR Experiments. DRIFT spectra, recorded after a 0.4-s, 350-nm irradiation of powdered PVG containing 3×10^{-4} mol of $Fe(CO)_5$(ads)/g of PVG under 100 Torr of 1-pentene (Figure 3), show a loss of the $Fe(CO)_5$(ads) bands at 2026 and 2004 cm^{-1}. New absorptions are immediately apparent at higher and lower frequencies, but their changes in intensity after photolysis are biased by the reappearance of 2026- and 2004-cm^{-1} bands of $Fe(CO)_5$(ads). As previously described, this is due principally to the replenishment of surface-depleted $Fe(CO)_5$(ads) by diffusion through the powdered glass in the microreactor.[13] Consequently, $Fe(CO)_5$(ads) spectra are substracted from spectra acquired at later times to reveal minor features in the photoproduct spectra.

Difference spectra recorded after pulsed 355-nm excitation with a Nd:YAG laser (50 mJ, 7 ns fwhm) show that bands at 2081,

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(28) Since the adsorbate is not uniformly distributed throughout the entire pore volume, surface coverage cannot be uniquely defined. Instead, a lower limit is calculated (see ref 13) where it is assumed that the surface area within the impregnated volume is 130 m^2/g and the area occupied by $Fe(CO)_5$(ads) is 0.3 nm^2.

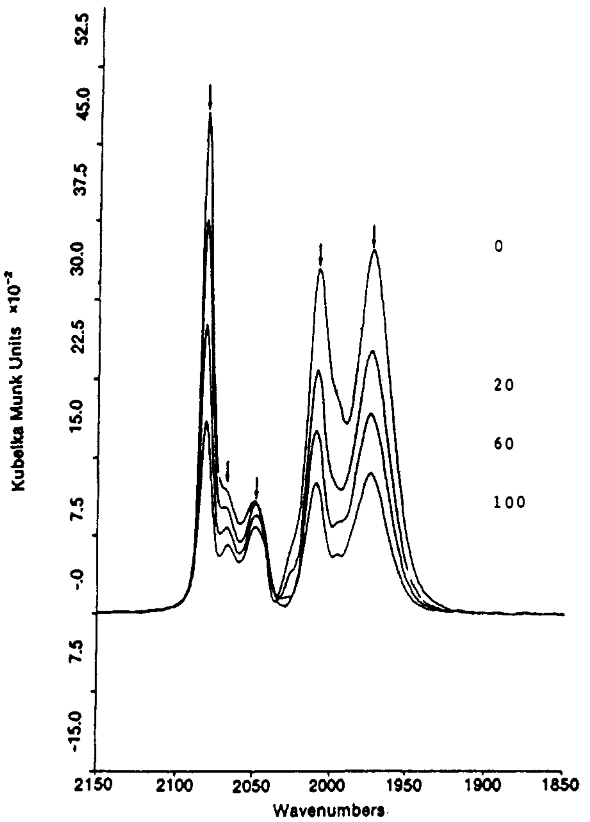

Figure 4. Difference spectra (see text) recorded immediately (0) and 20, 60, and 100 s after a 1.6-s, 350-nm irradiation of $Fe(CO)_5$(ads), 3×10^{-4} mol/g of PVG, under 100 Torr of 1-pentene. Numbers indicate the time in seconds, and arrows show the change in intensity after excitation.

2012, and 1973 cm^{-1} appear immediately during photolysis and decay within ca. 150 s after photolysis. Since the decays correlate with each other, these bands are assigned to a single photoproduct. Difference spectra recorded after a 0.4-s, 350-nm excitation with the Kr laser show the 2081-, and 2012-, and 1943-cm^{-1} bands as well as bands at 2068 and 2058 cm^{-1}. The bands at 2068 and 2058 cm^{-1} decay at different rates and are assigned to additional photoproducts. Increasing the 1-pentene pressure from 100 to 160 Torr has little effect on the product spectrum, but increasing the irradiation time causes marked changes in relative band intensity. A 1.6-s irradiation under 100 Torr of 1-pentene (Figure 4) results in the appearance of the 2081-, 2012-, and 1973-cm^{-1} bands along with a significant increase in the relative intensity of the 2068- and 2051-cm^{-1} bands and the appearance of less intense features at 2058, 2025, 2006, 1989, and ca. 1973 cm^{-1}. The increases in relative intensity of these secondary features, particularly the 2068- and 2051-cm^{-1} bands, occur at the expense of the 2081- and 2012-cm^{-1} bands. The change in the 1973-cm^{-1} band with increasing irradiation time is more complex. Following a 1.6-s irradiation, its thermal decay no longer correlates with that of the 2081- and 2012-cm^{-1} bands, and the band broadens relative to the 2081- and 2012-cm^{-1} bands. Although distinct shoulders are not discernible, it appears that the 1973-cm^{-1} band is composed of a number of absorptions. All absorptions decay after photolysis, indicating the formation of transient intermediates rather than stable photoproducts. None of the later appearing bands, however, decay with concurrent reappearance of bands indicative of $Fe(CO)_5$ or the initially formed 2081-, 2012-, and 1973-cm^{-1} bands. Overall, the spectral changes indicate that $Fe(CO)_5$(ads) is converted to a primary photoproduct that is then irreversibly converted to three transient photoproducts.

The induction period preceding alkene isomerization in fluid solution is associated with the conversion of the pentacarbonyl to $Fe(CO)_4(1\text{-}C_5H_{10})$, which is then photochemically converted to the catalyst.[6,10] Grant and co-workers attribute the absorbance that develops during the induction period at 348 nm to the initial formation of $Fe(CO)_4(1\text{-}C_5H_{10})$.[6] A 350-nm photolysis of $Fe(CO)_5$(ads) under 1-pentene results in the immediate uptake of 1-pentene (Figure 2) and the growth of an absorbance in the 350–360-nm region prior to alkene isomerization, DRIFT spectra show the immediate appearance of bands at 2081, 2012, and 1973 cm^{-1}, bands which, although the relative intensities differ, agree with the reported spectrum of $Fe(CO)_4(1\text{-}C_5H_{10})$. In 3-methylpentane at 25 °C, $Fe(CO)_4(1\text{-}C_5H_{10})$ exhibits bands at 2083, 2002, and 1981 cm^{-1}.[10] Consequently, the initial photochemical reaction on the glass is, as found in fluid solution

$$Fe(CO)_5(ads) + 1\text{-}C_5H_{10} \rightarrow Fe(CO)_4(1\text{-}C_5H_{10})(ads) \quad (1)$$

The quantum yield of decarbonylation of $Fe(CO)_5$ on PVG is essentially unity, 0.96 ± 0.05, and in vacuo the resulting tetracarbonyl undergoes rapid oxidative addition to the glass surface.[13] Yet, there is no indication in the electronic or the DRIFT spectra of the formation of $H\text{–}Fe(CO)_4\text{–}OH$ or $H\text{–}Fe(CO)_4\text{–}OSi$. Under 100 Torr of 1-pentene, $Fe(CO)_4(1\text{-}C_5H_{10})$(ads) formation is quantitative, which is somewhat surprising in view of the abundance of silanol groups, 4–7 groups/100 Å^2.[29,30] This is not the case with other alkenes. DRIFT spectra recorded after 350-nm photolysis of $Fe(CO)_5$(ads) under 100 Torr of ethylene, for example, show an immediate appearance of both $Fe(CO)_4(C_2H_4)$(ads) and $H\text{–}Fe(CO)_4\text{–}OSi$.[31] At the same alkene pressure, the flux of ethylene onto the surface is 1.6 times larger than the flux of 1-pentene onto the surface. If the rates of reaction between $Fe(CO)_4$(ads) and C_2H_4 and $1\text{-}C_5H_{10}$ are similar, then quantitative formation of $Fe(CO)_4(1\text{-}C_5H_{10})$, but not $Fe(CO)_4(C_2H_4)$, is inconsistent with reactions determined by the flux of the alkenes onto the surface. Rather, since the amount of 1-pentene adsorbed is larger than the amount of ethylene adsorbed, quantitative formation of $Fe(CO)_4(1\text{-}C_5H_{10})$ suggests that reaction 1 occurs principally between coadsorbed species.

Trapping experiments with trimethylphosphine establish rapid formation of $Fe(CO)_3$ following 350-nm laser excitation of $Fe(CO)_5$(ads).[13] Although the tricarbonyl is the so-called "mobile intermediate" that leads to dimer and trimer formation of PVG,[13] aggregation of the metal is not essential to catalytic activity on the glass. Bands in the bridging CO region, 1750–1800 cm^{-1}, or bands attributable to trimeric species are not detected at the onset of alkene isomerization. After 40 min of irradiation, UV–visible spectra do show a weak absorption at 605 nm that agrees with the $\sigma \rightarrow \sigma^*$ transition of $Fe_3(CO)_{12}$(ads). However, the absorbance change, which corresponds to the formation of $(3.5 \pm 0.2) \times 10^{-9}$ mol of $Fe_3(CO)_{12}$(ads)/g of PVG, occurs after the isomerization of ca. 70% of the initial 1-pentene (Figure 2). At least during its initial stages, catalytic activity on the glass is limited to more highly unsaturated, monometallic species derived from the photolysis of $Fe(CO)_4(1\text{-}C_5H_{10})$.

While it is agreed that the induction period reflects the stepwise generation of the catalyst, the identity of the catalytic intermediate in fluid solution remains controversial. Chase and Wigert assign a band at 1969 cm^{-1} to the active catalyst and report that its lifetime, which varies from 7 to 28 s, depends on the concentration of 1-pentene.[5] Grant and co-workers propose that the catalytic cycle is carried by mono(olefin)- and bis(olefin)-substituted iron tricarbonyl complexes with the phenomenological catalyst being $Fe(CO)_3(1\text{-}C_5H_{10})$.[6] Wrighton and co-workers also propose the involvement of a bis(olefin) complex.[10] Photolyses in low-temperature matrices, however, reveal bands assigned to the π-allyl complex $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ and support the proposal that the latter complex is the essential intermediate in the catalytic cycle.[10]

The spectral changes observed with the impregnated glass resemble those observed in low-temperature matrices.[10] Increasing the irradiation time broadens the 1973-cm^{-1} band and increases the intensities of the 2068-, 2051-, and 2025-, 2006-, and 1989-cm^{-1} bands. The increase in intensity of the last five bands occurs at the expense of the initial 2081-, 2012-, and 1973-cm^{-1} bands.

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Therefore, the later appearing bands are assigned to photoproducts derived from $Fe(CO)_4(1\text{-}C_5H_{10})$(ads). In low-temperature matrices, photolysis of $Fe(CO)_4(1\text{-}C_5H_{10})$ results in further CO loss.[10] Photolyses of $Fe(CO)_5$(ads) on PVG also establish multiple CO loss, and trapping experiments with trimethylphosphine establish $Fe(CO)_3$(ads) as the dominant photoproduct following 350-nm laser excitation.[13] Consequently, the secondary spectral features are assigned to photoproducts of lower CO content. Secondary CO loss, as opposed to alkene loss, is also consistent with the lack of thermal reversibility after photolysis. Unlike the more strongly adsorbed 1-pentene, the photodissociated CO rapidly desorbs from the glass[13] and prevents thermal regeneration of $Fe(CO)_4(1\text{-}C_5H_{10})$(ads) or $Fe(CO)_5$(ads).

The band at 2051 cm^{-1} and a component of the broadened 1973-cm^{-1} band are assigned to $Fe(CO)_3(1\text{-}C_5H_{10})_2$, since in 1-pentene at 195 K, $Fe(CO)_3(1\text{-}C_5H_{10})_2$ exhibits a band at 2048 cm^{-1} and a more intense band at 1972 cm^{-1}.[10] It should be noted, however, that the assignment is based principally on the wavelength similarity since, although changes in relative intensity are expected in view of the difference of the media, the complexity of the 1973-cm^{-1} band (Figure 4) precludes an accurate measure of relative intensities. The band at 2068 cm^{-1} and the shoulder at 1989 cm^{-1} are assigned to the π-allyl complex $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ since the latter complex exhibits bands of similar intensities at 2059 and 1989 cm^{-1} in a 90 K 1-pentene matrix.[10] The bands at 2025 and 2006 cm^{-1} (Figure 4) also develop with increasing irradiation time but always remain low-intensity shoulders. Unlike the bands assigned to the bis(olefin) and π-allyl complexes, which persist for about 100 s after excitation, the 2025- and 2006-cm^{-1} bands decay in $\leq$60 s. The correlation in decay rates suggests that the bands correspond to a single species, but their assignment is not possible with the available data. There is no evidence in our spectra of lower frequency bands, $\leq$1925 cm^{-1}, that are tentatively assigned to complexes of higher alkene content.[10]

The similarity of the spectral changes observed on PVG to those found in low-temperature hydrocarbon matrices suggests an equivalent reaction sequence where, as previously proposed,[6,10] the essential intermediates are either $HFe(CO)_3(\eta^3\text{-}C_5H_9)$ or $Fe(CO)_3(C_5H_{10})$. However, the data described above, in our opinion, do not identify the catalytic intermediate generated on PVG. There is no evidence in our spectra, for example, of the formation of a distinct 1969-cm^{-1} band, which Chase and Weigert assign to the catalytic intermediate in 1-pentene,[5] although it is possible that a similar band exists within the broadened 1973-cm^{-1} band. Nevertheless, the intermediate generated on PVG exhibits remarkable catalytic activity. Schroeder and Wrighton report a limiting quantum yield of isomerization of 429 ± 43 when the reaction is carried out in neat 1-pentene with 366-nm excitation.[7] Subsequent experiments by Mitchener and Wrighton using 351-nm laser excitation yield an isomerization quantum yield of 68 in neat 1-pentene.[8] Under similar conditions, Grant and coworkers report an isomerization quantum yield of 800 with pulsed 337- or 351-nm excitation.[6] On the basis of the light intensity, typically 2×10^{-9} einstein/(s cm^2), incident on optically dense samples, i.e. containing 1.86×10^{-5} mol of $Fe(CO)_5$(ads) under 160 Torr of 1-pentene, the quantum yield of 1-pentene isomerization (*cis*- + *trans*-2-pentene) is 152 ± 23. The value is considerably less than that reported by Grant and co-workers[6] and a priori suggests a less active intermediate. Yet, our experiments were carried out under static conditions, i.e., an initial pressure of 1-pentene of 160 Torr. Furthermore, the data indicate that the reactions occur principally between coadsorbed reagents, which further limits the amount of immediately available 1-pentene to ca. 1.5×10^{-4} mol adsorbed/g of PVG. Since the quantum yield of isomerization is dependent on the concentration of 1-pentene, the activity of the catalyst generated on PVG, considering the limitations imposed by the heterogenity of the system, is certainly similar to that generated in neat 1-pentene.

In benzene solution, the trans/cis product ratio is within experimental error of the expected thermodynamic ratio. This result as well as the high quantum yield for isomerization led to the conclusion that light generates the active species, but the actual alkene isomerization is a thermal event promoted by a ground-state species.[7] The spectral similarities and the high quantum yield of isomerization, 152 ± 23, suggests a similar sequence on the glass. Light generates the active species, which then thermally catalyzes the alkene isomerization. With the adsorbed reagents, however, the product ratio varies with irradiation time. Figure 2, for example, yields 1.62 for the trans/cis ratio, when measured after 10 min, and 3.56, when measured after 60 min. The measured ratios vary, but the pattern is reproducible from sample to sample. With samples initially containing 1.8×10^{-5} mol of $Fe(CO)_5$(ads)/g of PVG under 160 Torr of 1-pentene, ratios measured within the first 10 min of reaction are 1.6 ± 0.2 and increase to 3.7 ± 0.2 after 60 min.

The latter value is similar to that reported in fluid solution,[7] but as found with other hybrid systems,[11,12] the initial product ratios differ substantially from the expected thermodynamic ratio, 4.82.[32] The reasons for this initial bias are not clear. The later appearance of $Fe_3(CO)_{12}$(ads) indicates an evolution of the species generated on the glass; i.e., the later formed species are not equivalent to those initially formed. Yet, the largest difference from the expected ratio occurs when the adsorbed transients spectrally resemble those found in low-temperature hydrocarbon matrices. On the other hand, the alkenes quantitated by the GC method are those in the surrounding vapor phase. One possibility is that the initial difference in product ratio reflects differences in alkene adsorptivity rather than an actual bias in product ratio imposed by this hybrid catalyst.

Conclusion. Photolysis of $Fe(CO)_5$(ads) under 1-pentene yields $Fe(CO)_5(1\text{-}C_5H_{10})$(ads), which is then photochemically converted to the shorter lived $Fe(CO)_3(1\text{-}C_5H_{10})_2$(ads) and $HFe(CO)_3(\eta^3\text{-}C_5H_9)$(ads). Although the last two species are thought to be crucial intermediates in the homogeneous catalytic systems, further experiments are necessary to establish the active species on the glass. Nevertheless, the quantum yield of isomerization indicates that the mononuclear, thermal catalyst generated in this hybrid system exhibits an activity similar to that found in homogeneous media.

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Registry No. $Fe(CO)_5$, 13463-40-6; $Fe(CO)_4(1\text{-}C_5H_{10})$, 58614-17-8; $Fe(CO)_4(C_2H_4)$, 32799-25-0; $Fe(CO)_3(1\text{-}C_5H_{10})_2$, 115183-52-3; $HFe(CO)_3(\eta\text{-}C_5H_9)$, 84521-04-0; 1-pentene, 109-67-1; ethylene, 74-85-1.

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