cooling. After the solution has been stirred for 10 min at room temperature, methyl iodide (1.21 mL, 20 mmol) is added. The reaction mixture is worked up by addition of H_2O and CH_2Cl_2. After the dichloromethane extract has been washed with water, dried over Na_2SO_4, and concentrated, the products are purified by filtration through silica gel with hexane:benzene (1:1) to give **14** as a colorless oil: yield 1.86 g (93.9%); IR (KBr) ν_{max} 3050, 2940, 1580, 1450, 1430, 1370, 1170, 1055, 1020, 800, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3 H), 0.58 (s, 3 H), 2.10 (s, 3 H), 2.70 (dd, 1 H, J = 11 Hz, 4 Hz), 6.72 7.20 (m, 5 H), 7.68 (dd, J = 7 Hz, 1.5 Hz); mass spectrum (m/e), 282 (M^+). Anal. Calcd for $C_{19}H_{22}S$: C, 80.79; H, 7.85. Found: C, 81.57; H, 7.88.

Preparation of Sulfonium Salt 15. To a suspension of dimethoxycarbonium fluoroborate (2.1 g) in dichloromethane (5 mL) is added a solution of **14** (1.76 g, 6.23 mmol) in dichloromethane (10 mL) held at −30 °C under an atmosphere of nitrogen. The mixture is allowed to warm to room temperature and is stirred for additional 4 h. Then, ethyl acetate (40 mL) was added, the mixture was stirred, and the solvent was decanted. Fresh ethyl acetate (20 mL) is added to the oily residue and it is stirred overnight. The resulting crystalline precipitate is collected and dried, giving **15** as colorless prisms: yield 1.3 g (54.4%); mp 225–230 °C dec; IR (KBr) ν_{max} 3425, 3040, 2940, 1580, 1430, 1050, 800, 760, 710 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.60 (s, 3 H), 0.65 (s, 3 H), 2.65–3.06 (m, 5 H), 2.92 (s, 6 H), 3.45 (dd, 1 H, J = 12 Hz, 4 Hz), 4.73 (dd, 1 H, J = 11 Hz, 4 Hz), 6.81–7.40 (m, 6 H). Anal. Calcd for $C_{20}H_{25}BF_4S$: C, 62.51; H, 6.56. Found: C, 62.52; H, 6.52.

Preparation of 8,16-Dimethyl[2.2]metacyclophan-1-ene (2). To a solution of patassium *tert*-butoxide (610 mg, 45 mmol) in tetrahydrofuran (30 mL) there is added with stirring sulfonium salt **15** (1.2 g, 3.12 mmol). After the reaction mixture has been stirred at room temperature under a nitrogen atmosphere for 4 h, benzene is added and the mixture is made acidic by addition of dilute aqueous hydrochloric acid. The organic layer is separated, washed with water, dried, and concentrated. The residue is recrystallized from methanol to give **2** as colorless needles: yield 700 mg (95.8%); mp 147–148 °C (lit.[3] mp 151–152 °C).

Registry No. 2, 28746-29-4; **4**, 61024-94-0; **5**, 92396-96-8; **6**, 92396-97-9; **7**, 92396-98-0; **9**, 92396-99-1; **10**, 92397-00-7; **11**, 92397-01-8; **12**, 92397-02-9; **13**, 92397-03-0; **14**, 92396-93-5; **15**, 92396-95-7; Na_2S, 1313-82-2.

C–H Insertion, Hydrogen Exchange, and Dimerization of Ethylene upon Condensation with Iron Atoms at 77 K and Subsequent Warming

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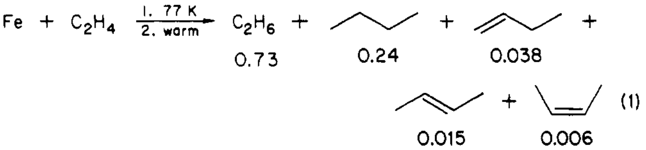
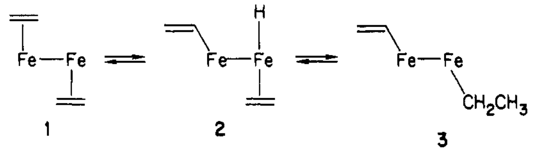
The interaction of an olefin with a metal center is of considerable interest in the areas of heterogeneous[1] and homogeneous catalysis[2] and surface chemistry.[3] In order to model this interaction between an alkene and an unsaturated metal center, we have investigated the reaction between iron atoms and ethylene at 77 K.

When iron atoms, generated by evaporating iron in a resistively heated molybdenum–alumina crucible, are cocondensed with ethylene and the resultant mixture is allowed to warm to room temperature, the products shown in eq 1, along with their relative yields, are obtained. Table I gives representative product yields under a variety of conditions.

Thus, the cocondensation of Fe and C_2H_4 brings about reduction, dimerization, and reductive dimerization of the ethylene. The fact that reduction is observed implicates an iron hydride which may be the result of an initial insertion of iron into a C–H bond as in eq 2. In order to asess the extent of such a process, a mixture of C_2H_4 and C_2D_4 (5 mmol of each) was cocondensed with iron. The infrared spectrum of the ethylene recovered from this reaction after warmup was essentially identical with that of a statistical mixture of the deuterated and protiated ethylenes. In order to rationalize this rapid exchange of vinylic hydrogens, we propose that an initial iron ethylene complex, **1**, undergoes insertion into a C–H bond to generate vinyl hydride **2** which can then insert another ethylene into the Fe–H bond to generate **3** as shown in eq 2.[4]



(1)



(2)

If this reaction is rapid and reversible, substitution of C_2D_4 for one of the ethylene molecules in eq 2 will lead to a statistical mixture of the deuterated and protiated ethylenes. This rapid exchange of vinylic hydrogens is reminescent of the work of Touroude and Gault who reported vinylic hydrogen exchange between propene-d_6 and a number of 1-alkenes on an iron surface at 236 K.[5] In the present study, we have also found that exchange will occur between ethylene and ethylene-d_4 on an iron surface. Thus, Fe atoms were condensed at 77 K and allowed to warm to room temperature, and the resultant surface was treated with a 1:1 mixture of C_2H_4 and C_2D_4 for 10 min. Analysis of the recovered ethylene again revealed statistical H–D scrambeling. These results are consistent with numerous spectroscopic studies of ethylene on a surface of iron[6] and other metals[7] in which loss of hydrogen to generate a surface-bound acetylene invariably occurs. A logical first step in such a process is the C–H insertion to generate a σ-vinyl intermediate as depicted in eq 2. Studies of the interaction of deuterium gas with alkenes on Ni and Fe surfaces have provided evidence for σ-vinyl intermediates similar to **2**.[8]

In another experiment, C_2D_4 was condensed with Fe followed by the addition of propene to the matrix after condensation. When this mixture was allowed to warm to room temperature and stand for 1 h, mass spectrometry indicated substantial deuterium incorporation into the propene. However, when this experiment was repeated

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[†] Permanent address: Departamento de Quimica, Universidad de Concepĉion, Casilla 3-C, Concepcion, Chile.

(1) Zakharov, V. A.; Yermakov, Y. I. *Catal. Rev.* **1979**, *19*, 67.

(2) Parhsall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

(3) Anderson, J. R.; Baker, B. G. "Chemisorption and Reactions on Metallic Films"; Andersen, J. R., Ed.; Academic Press: New York, 1971; Vol. 2, p 63.

(4) The mechanistic equations in which reactions are depicted as occurring on two metal centers are meant to be schematic representations of the mechanisms only. No firm evidence as to the nuclearity of the reactions has been obtained.

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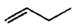
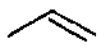
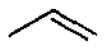
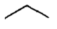
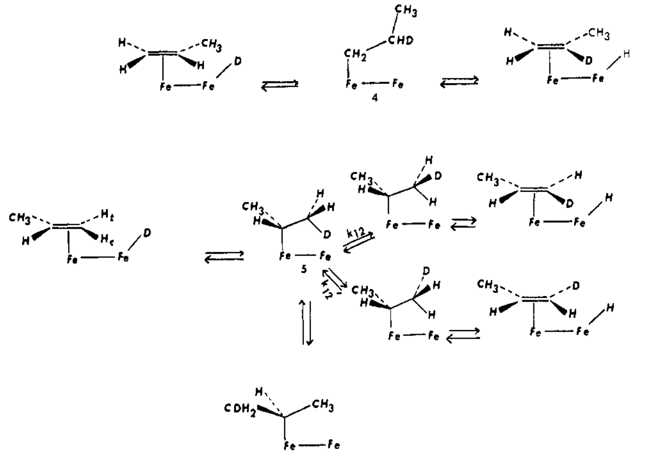
Table I. Products of the Iron-Ethylene Matrix in the Presence of Various Substrates

reactants (mmol)			recovered		product yields (mmol)				other	
C_2H_4	Fe	substrate added	C_2H_4	C_2H_6					products	(mmol)
10	3.2	none	7.7	0.32	1.0×10^{-1}	1.7×10^{-2}	6×10^{-3}	3×10^{-3}		
10	11.6	none	4.7	0.05	4.4×10^{-2}	1.3×10^{-2}	7.6×10^{-2}	4.1×10^{-2}		
10	14.1		5.9	0.40	6.0×10^{-2}		3.6×10^{-2}	1.8×10^{-2}		(6.85×10^{-1})
										(1.4×10^{-2})
10	1.9		a	a	a	2.84×10^{-1}	1.76×10^{-1}	1.42×10^{-1}		
10	11.9	CO (10 mmol)	5.4	0.59	1.64×10^{-2}	7×10^{-3}	2.2×10^{-2}	1.3×10^{-2}	$Fe(CO)_5$	(2×10^{-3})

[a] Not analyzed.

Scheme I



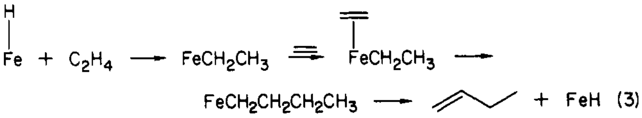
allowing the C_2D_4 and propene to remain in contact for only 10 min, the recovered propene contained less deuterium. In this case, the ^1H and ^{13}C NMR spectra showed that the deuterium had exchanged predominately into the vinylic positions of the propene. Integration of the 400-MHz ^1H NMR showed a ratio of H_{1c}:H_{1t}:H_2:H_3 of 2:2:1:10. This result indicates that H_2 exchanges twice as fast as H_{1c} and H_{1t} which exchange at equal rates. Further, the protons on C_1 exchange faster than those on C_3. These results are consistant with the mechanism in Scheme I in which, perhaps for steric reasons, the rate of addition of Fe to C_1 is faster than addition to C_2. Addition to C_1 generates **4** which can, upon loss of a proton, place deuterium on C_2. Addition of Fe to C_2 will generate **5** which may exchange H_{1c} or H_{1t} upon rotation about the C_1–C_2 bond and proton loss. The fact that H_{1c} and H_{1t} exchange at equal rates indicates that rotation about the C_1–C_2 bond occurs with equal facility in either direction ($k_{12} = k_{12}'$). In order for H_3 to exchange in **5**, one of the methyl hydrogens on C_3 must be transferred to the iron. Since exchange of H_{1c} and H_{1t} is 1.6 times faster than exchange of the three allylic hydrogens while statistical considerations demand that the allylic hydrogens in **5** exchange 1.5 times faster than those on C_1, we conclude that the methyl groups in **5** are nonequivalent. It is possible that the rotation about the C_2–Fe bond shown in Scheme I must occur before a hydrogen on C_3 can be transferred. If this is the case and the rate of this rotation is slow relative to exchange of H_{1c} and H_{1t}, the preference for exchange at C_1 over C_3 may be rationalized.

Additional evidence for insertion of Fe atoms into the C–H bond of ethylene upon condensation is provided by an experiment in which Fe is condensed with C_2H_4 and D_2O is added after condensation. In this case, the IR spectrum of the recovered ethylene shows ethylene-d_1 but no multiply deuterated ethylenes. We speculate that D_2O deuterates the Fe–C bond in **2** incorporating one deuterium and that the interaction of the D_2O with the iron surface deactivates it toward further reaction.

When carbon monoxide is added to the Fe–C_2H_4 matrix after condensation, small amounts of iron pentacarbonyl are isolated (Table I). The fact that no ethyleneiron tetracarbonyl[9] can be detected may argue against the intermediacy of a mononuclear iron–ethylene complex in these investigations. In this connection, it is interesting to note that Fe_2 inserts into the C–H bond of methane at 20 K[10] while Fe inserts only upon photolysis.[11]

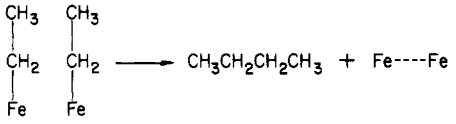
The ethane, which is invariably produced when iron and ethylene are cocondensed, most probably is the result of reduction of the ethylene by iron hydrides such as **2**. That the iron hydrides generated in these reactions are capable of effecting the reduction of added alkenes is indicated by the addition of propene to the Fe–C_2H_4 matrix. This experiment results in the formation of propane as well as the products in eq 1 (Table I).

The butenes, which result from a dimerization of the ethylene, may be rationalized according to the conventional mechanism for this reaction[12] shown in eq 3. In this case,



$$\underset{\text{Fe}}{\overset{\text{H}}{|}} + C_2H_4 \longrightarrow FeCH_2CH_3 \rightleftharpoons \underset{FeCH_2CH_3}{\overset{=}{|}} \longrightarrow FeCH_2CH_2CH_2CH_3 \longrightarrow \quad + \text{FeH} \qquad (3)$$

the initial product is postulated to be 1-butene which is partially isomerized to the 2-butenes by a series of hydride additions and eliminations. We can demonstrate that the iron–ethylene matrix can bring about the isomerization of 1-butene by condensing Fe and C_2H_4 and adding 1-butene to the matrix. When this matrix is allowed to warm to room temperature and stand for 1 h, the 1-butene is 53% isomerized to a mixture of (*E*)- and (*Z*)-2-butene (Table I). Butene isomerization by iron surfaces has been previously observed.[13] The butane generated in this reaction most likely results from a reduction of some of the butenes by the iron hydrides and by reductive elimination of two iron ethyl groups as shown in eq 4.



$$\begin{matrix} CH_3 & CH_3 \\ | & | \\ CH_2 & CH_2 \\ | & | \\ Fe & Fe \end{matrix} \longrightarrow CH_3CH_2CH_2CH_3 + \text{Fe----Fe} \qquad (4)$$

These experiments demonstrate that vinylic C–H insertion occurs upon condensation of iron with ethylene. The iron hydride generated in this manner is capable of effecting a number of reactions including hydrogen exchange, hydrogenation, and olefin dimerization.

Since condensation of C_2H_4 on a preformed surface of Fe results in hydrogen exchange (vide supra) but no di-

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[9] Murdoch, H. D.; Weiss E. *Helv. Chim. Acta* **1963**, *46*, 1588.

[10] Barrett, P. H.; Pasternak, M.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 222.

[11] Billups, W. E.; Konorski, M. M.; Hauge, R. H.; Margrove J. L. *J. Am. Chem. Soc.* **1980** *102*, 7393.

[12] Reference 2, pp 59–63.

[13] Touroude, R.; Gault, F. G. *J. Catal.* **1974**, *32*, 294.

merization or hydrogenation, we conclude than an initial Fe–C_2H_4 matrix is required for these reactions to occur. When finely divided iron powder is generated by the sodium amalgum reduction of $FeCl_2$ in THF in the presence of ethylene, no dimerization or hydrogenation of the ethylene is observed.

Experimental Section

Starting Materials. Ethylene, propenes, and the butenes were used as received from Matheson Gas products. The iron used was iron filings (degreased) from Matheson Coleman and Bell and was heated above its melting point (1808 K) under high vacuum for 3 min prior to evaporation. Ethylene-d_4 was purchased from Merck and Co. Deuterium oxide was obtained from Stohler Isotope Chemicals. Gas Chromatographic analyses of hydrocarbon products were carried out on a 20-ft dimethylsulfolane column with a Carle micro detector. Infrared measurements were carried out on a Perkin-Elmer Model 983 spectrometer. ^1H nuclear magnetic resonance spectra were measured on a Bruker 400 MHz spectrometer while ^{13}C spectra were run on a Nicolet 300-MHz instrument. Gas chromatography–mass spectrometry was carried out with a Dupont 491b spectrometer interfaced with a Varian 2700 GC and Finnigan data system.

General Procedure for the Reaction of Iron Atoms with Ethylene. The metal atom reactor is based on that described by Timms[15] in which Fe atoms are evaporated from a resistively heated molybdenum alumina crucible under high vacuum and deposited on the walls of a 2-L flask at 77 K. The crucibles are prepared by coating a spiral of 50-mil Mo wire (H. Cross Co.) with an aqueous suspension of alundum cement (Fischer), drying sucessively at 473 K and 973 K, and finally by passing a current of 55 A through the Mo wire under vacuum. In a typical experiment, 3–18 mmol of Fe are evaporated over a 30-min period and cocondensed with 10 mmol of C_2H_4. If an additional substrate is to be added, it is distilled into the reactor after cocondensation of iron and ethylene. The reactor is allowed to warm to room temperature and stand for 1 h. The volatile products are pumped from the reactor through traps at 133 K and 77 K. The 77 K trap contains mainly recovered ethylene and ethane which is quantitated by IR spectroscopy. The 133 K trap contains the remaining hydrocarbons which are identified by IR spectroscopy and mass spectrometry and quantitated by GC.

Analysis of Deuterated Products. A statistical mixture of the deuterated and protiated ethylenes was prepared by the procedure of Paul[16] which involved the reduction of a 1:2:1 mixture of C_2H_2, C_2HD, and C_2D_2 with Cr^{2+} in 1:1 H_2SO_4 and D_2SO_4. The IR spectrum of this mixture was similar to that obtained from cocondensation of Fe with 1:1 C_2H_4 and C_2D_4. When D_2O was added to the Fe–C_2H_4 matrix, C_2H_3D was identified in the recovered ethylene by its IR band at 809 cm^{-1}.[17] No other deuterated ethylenes could be detected in the IR. The deuterium content of the propene recovered from the Fe–C_2D_4 matrix was evaluated from its 400-MHz ^1H NMR spectrum.

Reduction of Ferrous Chloride in the Presence of Ethylene. Ferrous chloride (0.5 g, 4.3 mmol) and naphthalene (0.2 g, 1.5 mmol) were dissolved in 50 mL of dry THF. The solution was frozen at 77 K and degassed, and 1% Na(Hg) (0.5 g, 21 mmol of Na) was added. This mixture was then allowed to warm in the presence of 10 mmol of ethylene with stirring. The production of finely divided Fe powder was complete within 5 min of warming. The mixture was allowed to stir for an additional 1 h and the ethylene was analyzed in the usual manner. No ethane or C_4 hydrocarbons were detected.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are grateful to Drs. William T. Evanochko and Charles Watkins for running the high-field NMR spectra. We thank Mr. Gitendra C. Paul for the preparation of the statistical mixture of protiated and deuterated ethylenes.

Registry No. Fe, 7439-89-6; C_2H_4, 74-85-1; H_2, 1333-74-0; C_2D_4, 683-73-8; D_2O, 7789-20-0; (*Z*)-2-butene, 590-18-1; ethane, 74-84-0; butane, 106-97-8; 1-butene, 106-98-9; ethylene-d_1, 2680-00-4; ferrous chloride, 7758-94-3; naphthalene, 91-20-3; (*E*)-2-butene, 624-64-6.

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[17] Crawford, B. L., Jr.; Lancaster, J. E.; Inskeep, R. G. *J. Chem. Phys.* **1952**, *21*, 678.

Molybdenum Atom Desulfurizations of Organosulfur Compounds

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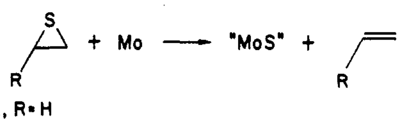
Received May 4, 1984

Molybdenum and its compounds are important constituents of a large number of desulfurization and hydrodesulfurization catalysts which are finding increasing utility in the removal of sulfur from fuels and their combustion products.[2] In order to investigate the initial interaction between molybdenum and sulfur in such processes, we have studied the reaction of a number of simple organosulfur compounds with atomic Mo.[3]

Since the molybdenum–sulfur bond is quite strong, it was anticipated that the use of highly energetic ($\Delta H_f = 659$ kJ/mol),[4] sterically nondemanding, and coordinatively unsaturated Mo atoms should effect the removal of sulfur from organosulfur compounds in a clean and straightforward manner. To a large extent these expectations were realized in that several organosulfur compounds gave sulfur-free hydrocarbon products. Not surprisingly, the efficiency of desulfurization was found to be critically dependent on the strength of the carbon–sulfur bond.

Results and Discussion

The reactions of Mo atoms with both cyclic and acyclic organosulfur compounds were carried out by cocondensing atomic Mo with the organic substrate at 77 K, allowing the mixture to warm to room temperature and analyzing volatile products. In the case of small-ring heterocycles, the expectation that relief of ring strain would lead to facile desulfurization was realized. Thus, when Mo atoms were cocondensed with thiirane, **1a**, and 2-methylthiirane, **1b**, the corresponding alkenes were generated in 132% and 119% yield, respectively, based on Mo vaporized, as shown in eq 1. In this and all cases, the molybdenum and sulfur



(1)

1a, R = H
1b, R = CH_3

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[2] (a) Hargreaves, A. E.; Ross, J. R. H. *J. Catal.* **1979**, *56*, 363. (b) Massoth, F. E.; Kibby, C. L. *J. Catal.* **1977**, *47*, 300. (c) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, 4, 245. (d) Desikan, P.; Amberg, C. H. *Can. J. Chem.* **1964**, *42*, 843.

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