apparently formed with isobutane–HF, but the yield of the normal complex was much less than that with ethane, propane, and butane. The reverse complex is characterized by a small red shift in the H–F fundamental (23 cm$^{-1}$ in the case of $CH_4$–FH) and a very low H–F librational mode (130 cm$^{-1}$ for $CH_4$–FH) and the normal complexes by larger red shifts in the H–F mode (65 cm$^{-1}$ for $C_3H_8$–HF) and a higher H–F librational frequency (216 cm$^{-1}$ for $C_3H_8$–HF). The ethane–HF complex also exhibits a blue-shifted methyl-tilting mode, which is indicative of repulsions for a ligand positioned over the C–C bond. Complexes with a 1:2 alkane–HF stoichiometry were formed on diffusion of HF and support the structure of the different 1:1 complexes with each hydrocarbon.

There are at least two factors at work that favor the switch from a reverse to normal complex in the alkane series $CH_4$ to $C_4H_{10}$. The hydrogen becomes progressively less positively charged as the chain length increases,[29] reducing the dipole interaction between the alkane hydrogen and the fluorine atom of HF, and the available C–C bond with a slight excess of negative charge becomes more polarizable with substitution of electron-donating methyl groups. If these complexes were all of the reverse structure, the HF fundamental shift would decrease with decreasing hydrocarbon acidity, which is not the case. The electron-donating property of the methyl group is clearly seen in the alkane complexes where the HF stretch shifts 24 cm$^{-1}$ more in the propane–HF complex relative to the ethane–HF complex, indicating an increased interaction with HF. Accordingly, the C–C bond is the preferred site of attachment for the acid HF.

The ab initio calculations presented show that methane forms a reverse HF complex with a small amount of charge density donated from HF to methane and that the ethane–HF complex involves a primary interaction between the acid hydrogen and the C–C bond and a secondary interaction between fluorine and one ethane hydrogen. The hydrogen bond lengths for the weak alkane complexes are longer than other stronger complexes; the $CH_4$–HF length is 2.67 Å while the two C–HF distances are 2.55 and 2.85 Å in the ethane complex. The relatively long hydrogen bond length in the latter complex is a result of repulsion between the alkane hydrogens and the hydrogen of HF, and at a distance of 2.3 Å, the complex is not bound.[30] The matrix infrared spectra and ab initio calculations show that definite long-range forces operate between alkanes and HF, which lead to weak complexes with defined structures. These studies provide a useful starting point for more accurate spectroscopic measurements, structure determinations, and theoretical calculations.

The HF absorptions due to the 1:1 complexes in a neon matrix are all higher than those in an argon matrix and frequency differences (argon to neon) range from 15 cm$^{-1}$ for the M–HF complex to 47 cm$^{-1}$ for the P–HF complex. This difference is due to the increased polarizability of argon compared to neon as the gas-to-matrix shift is due in part to dipole–induced dipole interactions. From this information and neon and gas-phase data on $N_2$–HF,[14,15,31] we predict the gas-phase HF stretches in the simple alkane complexes to be between 3900 and 3930 cm$^{-1}$.

**Acknowledgment.** Financial support from N.S.F. Grant CHE 85-16611 and the Academic Computing Center of the University of Virginia and helpful consultations with C. Trindle are gratefully acknowledged.

**Registry No.** HF, 7664-39-3; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; *n*-butane, 106-97-8; isobutane, 75-28-5.

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(30) Sapse, A. M., personal communication, 1986.

(31) Kolenbrander, K. D.; Lisy, J. M. *J. Chem. Phys.* **1986**, *85*, 2463.

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# Infrared Spectroscopy and Photochemistry of Iron–Ethylene Oxide in Cryogenic Matrices. The FTIR Spectrum of Vinyliron Hydroxide

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**Abstract:** The mechanism of the cryogenic reaction between an iron atom and an ethylene oxide molecule has been delineated. Iron spontaneously inserted into the carbon–oxygen bond of the cyclic molecule and formed the first unligated metallaoxetane. Upon visible photolysis of ferraoxetane, a metathesis reaction was observed where cleavage occurred through the iron–carbon and the carbon–oxygen bonds of the metallacycle. UV photolysis of the reaction intermediate, an iron oxide π-complexed to ethylene, led to the activation of one of the C–H bonds of ethylene and the formation of the final product, vinyliron hydroxide. Similar reaction pathways were observed for the diiron molecule reaction with ethylene oxide. Evidence for the double insertion of two iron atoms into the C–O bonds of ethylene oxide and the subsequent formation of a five-membered oxametallacycle ring has been seen through the detection of frequencies characteristic of an Fe–O–Fe stretching mode and a carbon–carbon stretching mode in the case of the perdeuterio product.

## I. Introduction

The interactions or the reactions between metal atoms and organic molecules in cryogenic matrices may lead to species that are similar to the reaction intermediates that occur in biological systems. The identification of the vibrational spectra of these transient species via FTIR matrix isolation spectroscopy will help delineate reaction mechanisms where the formation of such intermediates has been proposed. For instance, the mechanism of the oxygen transfer event in the catalytic cycle of cytochrome P-450 has been the subject of many studies. In an effort to study the intermediates proposed or speculated to be formed in such reactions, Groves and co-workers[1-3] used substrate molecules to

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(1) Groves, John T.; Haushalter, Robert C.; Nakamura, Mikio; Nemo, Thomas E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(2) *Cytochrome P-450. Structure, Mechanism and Biochemistry*; Ortiz de Montellano, Paul R., Ed.; Plenum: New York, 1986.

0002-7863/87/1509-4775$01.50/0

**Table I.** FTIR Frequencies ($cm^{-1}$) Measured for Ethylene Oxide in Solid Argon

| symmetry of mode | vib mode | $C_2H_4O^a$ | $C_2D_4O^a$ |
|---|---|---|---|
| $a_1$ | $\nu_1$ $CH_2$ or $CD_2$ s-stretch | 3020.2 (m) | 2212.9 (m) |
| | $\nu_2$ $CH_2$ or $CD_2$ scis | 1495.8 (w) | 1311.8 (m) |
| | $\nu_3$ ring stretch | 1273.3 (s) | 1014.8 (w) |
| | $\nu_4$ $CH_2$ or $CD_2$ wag | 1125.7 (w) | 966.2 (s) |
| | $\nu_5$ ring deform | 877.2 (vs) | 754.5 (vs) |
| $b_1$ | $\nu_9$ $CH_2$ or $CD_2$ s-stretch | 3010.3 (s) | 2180.6 (s) |
| | $\nu_{10}$ $CH_2$ or $CD_2$ scis | 1469.7 (w) | |
| | $\nu_{11}$ $CH_2$ or $CD_2$ wag | 1153.9 (w) | 962.5 (w) |
| | $\nu_{12}$ ring deform | 879.1 (vs) | 810.9 (m) |
| $b_2$ | $\nu_{13}$ $CH_2$ or $CD_2$ a-stretch | 3071.1 (s) | 2324.8 (s) |
| | $\nu_{14}$ $CH_2$ or $CD_2$ twist | 1146.5 (vw) | 898.7 (w) |
| | $\nu_{15}$ $CH_2$ or $CD_2$ rock | 821.5 (m) | 586.0 (vw) |

[a] vw = very weak. w = weak. m = medium. s = strong. vs = very strong.

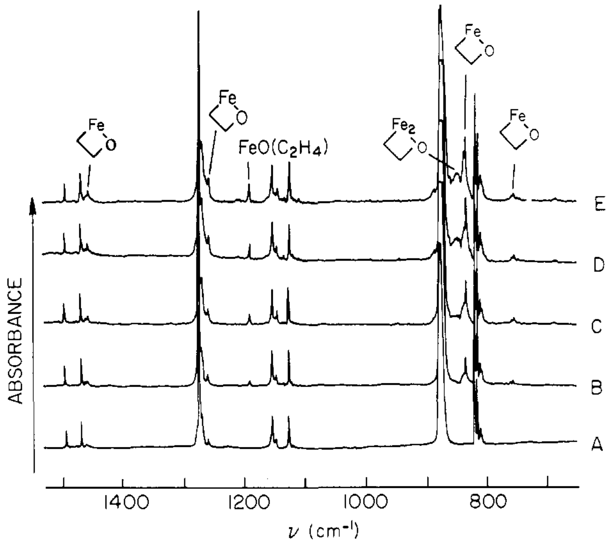

Figure 1. An iron concentration study. FTIR spectra of $Fe/C_2H_4O$ and $C_2H_4O$ in Ar. Molar ratios for $Fe:C_2H_4O:Ar$ = 0:5.2:1000 (A); 2.5:5.2:1000 (B); 4.9:5.2:1000 (C); 10.8:5.2:1000 (D); 14.7:5.2:1000 (E). The absorbance of the product peak (E) at 836.0 $cm^{-1}$ is 1.5. Spectral resolution = 1 $cm^{-1}$.

**Table II.** FTIR Frequencies ($cm^{-1}$) Measured for Ferraoxetane in Solid Argon

| $C_2H_4OFe$ | $C_2D_4OFe$ |
|---|---|
| 1457.9 | 1076.1 |
| 1259.5 | 1003.1 |
| 1138.0, 1134.9 | *924.5*,[a] 922.5 |
| 841.1, 839.1, *836.0*[a] | 749.5, 747.5 |
| 760.8, 757.6, 756.0 | |

[a] Frequencies given in italics belong to strongest absorptions for $C_2H_4OFe$ and $C_2D_4OFe$, respectively.

reveal the chemistry played by the oxidant. One mechanism suggested by Groves and co-workers[3] is the epoxidation of an olefin, namely, *trans*-1-deuteriopropylene, by a reconstituted cytochrome P-450 system which involves the formation of an oxametallacycle. On the basis of recent theoretical calculations, Sevin and Fontecave[4] have argued the formation of the metallacycle. However, they proposed that the metallacycle intermediate will be more favorable in systems possessing more degrees of freedom.

In the present study we have identified the FTIR spectrum of one of the simplest oxametallacycles, namely, ferraoxetane. This molecule was microsynthesized in a cryogenic argon matrix by the reaction of atomic iron with ethylene oxide. The photochemistry of this metallacycle was also studied. Excitation in the visible led to ring opening and the formation of an ethylene–iron monoxide $\pi$-complex through a metathesis mechanism. Upon UV photolysis, the metal oxide inserted into one of the inert C–H bonds of ethylene and vinyliron hydroxide was formed.

The metal atom activation of inert bonds of small cyclic organic molecules was observed for the first time in our laboratory when an iron atom was inserted into the C–C bond of cyclopropane.[5] Recent theoretical calculations on the mechanisms of cyclopropane ring opening by palladium showed that the edge palladation leading to the metallacyclobutane is favored over corner palladation.[6] An energy barrier equal to 17 kcal/mol was estimated showing the reaction to be endothermic by 6 kcal/mol.

## II. Experimental Section

A full description of the multisurface matrix isolation apparatus has been recently reported.[7] This machine was interfaced to an IBM–FTIR, Model IR98, vacuum spectrometer via a flange containing two rotatable sets of optical windows. A rotatable–translational matrix block was laid on top of the stationary closed-cycle helium refrigerator, an Air Products Displex Model CSW-202. The block temperature was usually maintained in the range 12.5–15 K. Three quartz crystal mass monitors have been mounted directly on the block to allow a precise measure of the molar ratios of metal, reactant, and matrix vapor species. During the matrix experiment the rate of metal deposition was monitored via a room-temperature water-cooled quartz crystal microbalance situated at the back of the furnace.

The heating element consisted of a 1-mil tantalum foil (Fansteel Metals) wrapped in a form of cylinder, 2.5 in. long by $^3/_8$ in. diameter. A $^3/_8$ in. OD tantalum tube was fitted and spot welded to this cylindrical foil at one end. At the other end the foil, cut in thin strips, was spotwelded to a $^5/_8$ in. OD tantalum tube. The alumina crucible containing iron (John Mathey, 99.9985% pure) was enclosed inside this vertical concentric furnace and was resistively heated to the vaporization temperature of the metal.

The matrix experiment consisted of simultaneous deposition of a beam of metal atoms with ethylene oxide (Matheson, 99.7%) or perdeuterioethylene oxide (MSD Isotopes, 98.0% isotopic purity) and excess argon (Matheson, 99.9995%) onto one of the 60 available polished rhodium-plated copper surfaces. The period of deposition was 30 min. Photolysis experiments were usually conducted subsequent to deposition by shining light from a 100-W medium-pressure short-arc mercury lamp via one of the side windows located in the furnace chamber. A water Pyrex filter with various Corning long-pass cutoff filters was used for photolysis in the visible range. A band filter, 280 $\leq \lambda \leq$ 360 nm, was employed in the ultraviolet region. After either deposition or photolysis, the block was rotated 180° and an FTIR single-beam spectrum was measured. Frequencies were obtained to an accuracy of ±0.05 $cm^{-1}$.

## III. Results

Before assigning any product peak that resulted from the interaction or reaction of iron with ethylene oxide in cryogenic matrices, the infrared spectrum of matrix-isolated ethylene oxide was measured and characterized in the 450–4000-$cm^{-1}$ region. Table I lists the observed frequencies ($cm^{-1}$) for all the infrared active modes of $C_2H_4O$ and $C_2D_4O$ in solid argon. Vibrational mode assignments were made by comparison to the gas-phase spectra.[8] Very small shifts (less than 1%) for most peaks were measured.

The cocondensation of iron with ethylene oxide in excess argon resulted in the growth of new absorption peaks. Figure 1 depicts spectra of these new product features in a metal concentration study where the molar ratio of ethylene oxide to argon was kept constant, namely, at 5.2 parts per thousand. The atomic ratio of metal to argon was varied from 0 to 14.7 parts per thousand. A set of peaks with key features at 756.0, 836.0, 1259.5, and

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(3) (a) Groves, John T.; Watanabe, J. *J. Am. Chem. Soc.* **1986**, *108*, 507. (b) Groves, John T.; Avaria-Neisser, G. E.; Fish, K. M.; Imachi, M.; Kuckowsky, Robert L. *J. Am. Chem. Soc.* **1986**, *108*, 3837.

(4) Sevin, A.; Fontecave, M. *J. Am. Chem. Soc.* **1986**, *108*, 3266.

(5) Kafafi, Zakya H.; Hauge, Robert H.; Fredin, Leif; Billups, W. Edward; Margrave, John L. *J. Chem. Soc., Chem. Commun.* **1983**, 1230.

(6) Bäckvall, Jan-E.; Björkman, Eva E.; Petterson, Lars; Siegbahn, Per; Strich, Alain *J. Am. Chem. Soc.* **1985**, *107*, 7408.

(7) Hauge, Robert H.; Fredin, Leif; Kafafi, Zakya H.; Margrave, John L. *Appl. Spectrosc.* **1986**, *40*, 588.

(8) Shimanouchi, Takehiko *Tables of Molecular Vibrational Frequencies*; National Bureau of Standards: Washington, D.C., 1971; Vol. 1, pp 87–88.

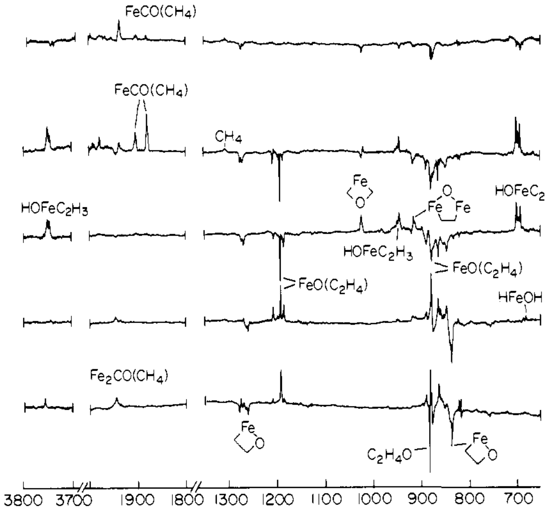

**Figure 2.** A photolysis study. FTIR difference spectra of Fe/$C_2H_4O$ reaction intermediates in solid argon. Molar ratio of Fe:$C_2H_4O$:Ar = 4.9:5.2:1000. (A) No photolysis; (B) $\lambda > 500$ nm, 10 min; (C) $\lambda > 400$ nm, 10 min; (D) 4 min, (E) 1 h, (F) 4 h, 280 nm $< \lambda <$ 360 nm.

1457.7 cm$^{-1}$ appeared under dilute conditions. This set kept the same relative intensities as the metal concentration was varied. This group of bands was assigned to a product with the molecular formula $C_2H_4OFe$, since it was predominant at the atomic iron and monomeric ethylene oxide concentration regimes. The strongest absorptions of this molecule were located at 836.0, 839.1, and 841.1 cm$^{-1}$, respectively. A similar set of peaks was observed at 847.8, 850.5, and 853.6 cm$^{-1}$ for the diiron analogue when the metal concentration was raised close to 1%. Table II lists the frequencies measured for $C_2H_4OFe$ and its perdeuterio analogue $C_2D_4OFe$ in solid argon.

In this paper emphasis will be on the photochemistry of the metal atom product. Figure 2 displays difference spectra of the Fe/$C_2H_4O$/Ar system that reflect spectral changes due to the photochemical rearrangements occurring as the matrix was photolyzed from the visible throughout the ultraviolet region using different filters and varying the period of photolysis. When the matrix was exposed to filtered light ($\lambda > 500$ nm) from the mercury lamp, the product bands were reduced and new absorption peaks grew in at 1480.3 1190.6, 887.4, 862.7, and 846.4 cm$^{-1}$. Photolysis with shorter wavelength light, $\lambda > 400$ nm, caused the total depletion of the initial product bands and further growth of the photoproduct peaks. The identity of this new species was not initially recognized until a matrix study was carried out on the iron/ethylene cryogenic reactions and interactions.[9] A comparison of the spectrum of this photoproduct with that of iron–ethylene π-complexes revealed the identity of this photoproduct; it was obvious that a similar π-complex was formed in this photoreaction. This conclusion was further supported by deuterium labeling experiments that gave the characteristic spectrum with the expected isotopic shifts for a π-complex. Figure 3 shows difference FTIR spectra for Fe/$C_2D_4O$ in solid argon. Note that the peak at 862.7 cm$^{-1}$ showed a slight positive shift of the order of a few wavenumbers upon deuterium substitution. This frequency is very close to the Fe=O stretching frequency which is 873 cm$^{-1}$. The remaining spectrum of this photoproduct showed absorption peaks at 1297.4, 938.2, 722.7, and 658.8 cm$^{-1}$ characteristic of an ethylene π-complex. We thus assign this set of frequencies to $FeO(C_2D_4)$, an ethylene iron monoxide π-complex.

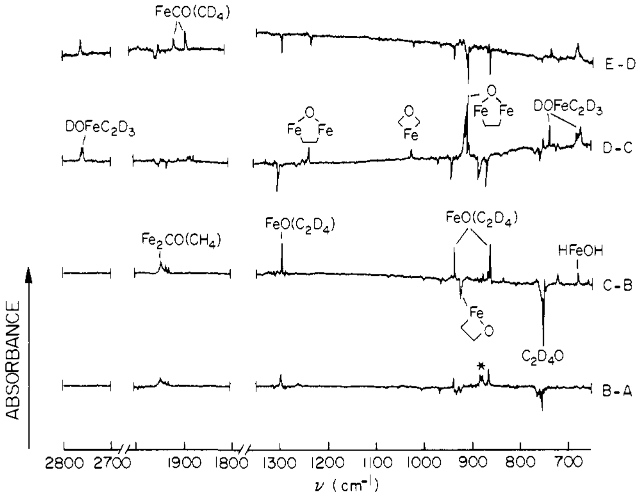

**Figure 3.** A photolysis study. FTIR difference spectra of Fe/$C_2D_4O$ reaction intermediates in solid argon. Molar ratio of Fe:$C_2D_4O$:Ar = 3.9:3.7:1000. (A) No photolysis; (B) $\lambda > 500$ nm, 15 min; (C) $\lambda > 400$ nm, 15 min; (D) 50 min, (E) 2 h, 280 nm $< \lambda <$ 360 nm. Peaks at 878.4 and 881.3 cm$^{-1}$ (indicated by an asterisk) have not been identified.

Upon UV photolysis the peaks associated with the π-complex were reduced with the concurrent growth of new absorptions mainly at 3749.7, 2917.1, 1556.3, 1439.4, 1019.0, 944.2, 699.6, 541.7 cm$^{-1}$ for Fe/$C_2H_4O$ and at 2762.3, 1484.9, 1066.7, 737.6, 681.5, 527.9 cm$^{-1}$ for Fe/$C_2D_4O$. Total bleaching of the π-complex was achieved in a period close to 1 h. The UV photoproduct has absorptions in the O–H (3749.7 cm$^{-1}$), Fe–O (699.6 cm$^{-1}$), and probably the Fe–C (541.7 cm$^{-1}$) stretching regions. Furthermore, frequencies characteristic of a vinyl moiety were also observed. We thus propose that UV photolysis caused the photorearrangement of the ethylene iron monoxide π-complex and led to the insertion of the iron monoxide molecule into one of the C–H bonds of ethylene. A new compound has been formed, namely, vinyliron hydroxide.

A group of bands located at 1022.1, 916.0, 913.9, and 911.2 cm$^{-1}$ grew in with short UV photolysis and disappeared with prolonged irradiation. A similar set with very small isotopic shifts was observed at 1021.8, 912.9, 909.8 with a feature at 1235.4 cm$^{-1}$ for the Fe/$C_2D_4O$/Ar system. The peaks at 1022.1 cm$^{-1}$ for Fe/$C_2H_4O$ and 1021.8 cm$^{-1}$ for Fe/$C_2D_4O$ were not related to the other bands. They decreased in intensity with further UV photolysis with the growth of peaks with frequencies very close to iron monocarbonyl as well as methane in the case of $C_2H_4O$. A possible candidate for the peaks in the 900-cm$^{-1}$ region is a double insertion iron product with an FeOFe group and a bridging ethylene. The frequencies observed in this region are characteristic of an FeOFe stretching mode as observed for both HFeOFeH and DFeOFeD at 914.5 and 911.8 cm$^{-1}$, respectively.[12] The 1235.4-cm$^{-1}$ frequency could be assigned to the carbon–carbon stretching mode of $C_2D_4$. The double insertion of iron atoms into two neighboring inert bonds has been previously observed when two iron atoms inserted either into the two O–H bonds of $H_2O$[12] or into the O–H and the C–O bonds of $CH_3OH$[11] and formed HFeOFeH and $HFeOFeCH_3$, respectively.

Bands in the C≡O stretching region appeared with visible photolysis at 1927.7, 1934.3, 1942.0, and 1945.1 cm$^{-1}$. These frequencies are very close to those measured in our laboratory for $Fe_2CO$ at 1930.2, 1933.5, 1936.2, and 1946.3 cm$^{-1}$, respectively. UV photolysis led to the disappearance of these bands as well as the 1022.1-cm$^{-1}$ peak and growth of new bands in the C≡O stretching region of FeCO (1897.9, 1940.8 cm$^{-1}$) at 1880.0, 1881.7, 1905.3, and 1937.4 cm$^{-1}$ and the production of methane. A slight reduction in vinyliron hydroxide peaks was also observed.

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(9) Kafafi, Zakya H.; Hauge, Robert H.; Margrave, John L. *J. Am. Chem. Soc.* **1985**, *107*, 7550.

(10) Chang, Sou-Chan; Kafafi, Zakya H.; Hauge, Robert H.; Billups, W. Edward; Margrave, John L., unpublished results.

(11) (a) Park, Mingue; Hauge, Robert H.; Kafafi, Zakya H.; Margrave, John L. *J. Chem. Soc., Chem. Commun.* **1985**, 1570. (b) Park, Mingue; Hauge, Robert H.; Kafafi, Zakya H.; Margrave, John L., unpublished results.

(12) Kauffman, James W.; Hauge, Robert H.; Margrave, John L. *J. Phys. Chem.* **1985**, *89*, 3541.

(13) Kauffman, James W.; Hauge, Robert H.; Margrave, John L. *High Temp. Sci.* **1984**, *17*, 237.

**Table III.** FTIR Frequencies (cm$^{-1}$) Measured for Ethylene Iron Monoxide $\pi$-Complex in Solid Argon

| approx type of vib mode | FeO($C_2H_4$) | FeO($C_2D_4$) |
|---|---|---|
| C=C stretch | 1485.4, *1480.3* | 1297.4 |
| $CH_2$ or $CD_2$ scis | 1205.8, 1195.9<br>*1190.6*,[a] 1185.6 | 938.2 |
| $CH_2$ or $CD_2$ wag | 887.4 | 722.7 |
| Fe=O stretch | *862.7*,[a] 859.9 | 868.3, *864.2*[a] |
| $CH_2$ or $CD_2$ wag or rock | 846.4 | 658.8 |

[a] Frequencies given in italics belong to most intense peaks within the group.

However, the partial disappearance of the latter was not related to the growth of these perturbed iron and diiron carbonyl peaks.

No photochemistry was observed in experiments carried out in neat ethylene oxide matrices.

## IV. Discussion

The present study deals with the reactivity of an iron atom toward an ethylene oxide molecule in an argon matrix. Experimental results suggest that the metal atom attacks the cyclic molecule mainly through the carbon–oxygen bond. The newly formed metallacycle undergoes a metathesis reaction where the Fe–C and C–O bonds are broken. The product is an ethylene molecule interacting through its $\pi$-system with an iron monoxide molecule. UV excitation of this $\pi$-complex leads to its photorearrangement which causes the activation of one of the inert C–H bonds of ethylene. A new molecule, vinyliron hydroxide, is thus microsynthesized under cryogenic conditions.

**(i) Infrared Spectroscopy. (a) Ferraoxetane, $C_2H_4OFe$.** The cocondensation of atomic iron with ethylene oxide in excess argon led to the growth of new infrared peaks indicative of a new product being formed. Since the reaction was spontaneous, one may at first think that this product is just a simple adduct between the metal atom and the organic molecule. However, comparison between the spectra of free ethylene oxide and this product and their respective deuteriated analogues did not show any correlation. The lack of similarity between the two spectra and the fact that the product was found to be a precursor to the ethylene iron oxide $\pi$-complex (see the following section) suggests that this new infrared spectrum belongs to the C–O insertion product, ferraoxetane. Unfortunately, there is no IR spectrum known for a ligand-free metallaoxetane for comparison and verification of the identity of this new species.

This molecule will have either $C_s$ or $C_1$ symmetry depending on whether the ring is planar or nonplanar. Very little can be said about the geometry and structure of this molecule on the basis of the measured infrared spectrum alone. Theoretical calculations are thus needed for structural elucidation. Detailed isotopic studies with carbon-13 and oxygen-18 labeling experiments may help shed some light on the nature of the vibrational modes of some of the observed frequencies listed in Table II.

**(b) Ethylene Iron Monoxide $\pi$-Complex, FeO($C_2H_4$).** Table III lists the measured frequencies for the FeO($C_2H_4$) and FeO($C_2D_4$) complexes. The infrared spectrum exhibited by this molecule is characteristic of an ethylene $\pi$-complex. The interaction of the iron monoxide molecule with ethylene has led to the activation and large frequency shifts of the $\nu$(C=C) stretching and the $\delta$($CH_2$) symmetric bending modes of ethylene. These modes are known to be strongly mixed.[9] Since the $\nu$(C=C) and $\delta$($CD_2$) modes do not mix substantially in the case of $C_2D_4$, the frequency shift of the $\nu$(C=C) mode of FeO($C_2D_4$) relative to unperturbed $C_2D_4$ may give a more accurate measure of the weakening of the C=C bond of ethylene as a result of $\pi$-coordination to the metal oxide. This shift has been measured to be 221.0 cm$^{-1}$, a 14.6% decrease in frequency, reflecting a considerable decrease in the double bond order of the ethylene carbon–carbon bond. This shift is of the same order of magnitude as those measured for the different iron/ethylene $\pi$-complexes, namely Fe($C_2H_4$)$_2$, $Fe_2$($C_2H_4$), and $Fe_2$($C_2H_4$)$_2$. Table IV compares frequencies measured for the ethylene–iron and –diiron $\pi$-complexes to the ethylene–iron monoxide $\pi$-adduct. It is interesting to note that the perturbation caused by an iron monoxide molecule on ethylene gives rise to an infrared spectrum similar to those of Fe($C_2H_4$)$_2$ and $Fe_2$($C_2H_4$)$_{1,2}$ $\pi$-complexes. A similar kind of interaction is thus operative in all these cases. By comparing the Fe=O stretching frequency of FeO($C_2H_4$) to that of free FeO (873.0 cm$^{-1}$), a negative shift equal to 10.3 cm$^{-1}$ was measured. This was in contrast to the positive shift observed for FeO($N_2$).[10] In the former case $\pi$-interaction with the olefin seemed to withdraw electron density from the Fe=O double bond whereas in the latter case interaction with the $N_2$ molecule resulted in transfer of electron density to the metal oxide and thus strengthened its bond.

**(c) Vinyliron Hydroxide, $HOFeC_2H_3$.** The ultraviolet excitation of the ethylene iron monoxide $\pi$-complex resulted in its photorearrangement where the metal oxide inserted into one of the inert C–H bonds of ethylene and vinyliron hydroxide was formed. Table V lists the measured frequencies of $HOFeC_2H_3$ and $DOFeC_2D_3$, respectively. The spectral identification of this new exotic molecule was fairly straightforward. The observation of the O–H and Fe–O stretching frequencies signaled the presence of an iron hydroxide moiety. The vinyl group was characterized through measured frequencies of the C=C and the C—H stretching and the $CH_2$ deformation modes. By linking the vinyl group to iron hydroxide, one arrives at vinyliron hydroxide. The measured iron–carbon stretching frequency further confirmed this assignment. Table V also compares some of the frequencies measured for new molecules produced via the respective C–H, C–O, and O–H bond activation of ethylene,[9] methanol,[11] and water[12] by iron atom with those of vinyliron hydroxide. It is interesting to note that the frequencies measured for the vinyl group of vinyliron hydride and vinyliron hydroxide agree very well. The same is true for the hydroxide stretching frequency of vinyl-, methyl-, and hydridoiron hydroxides. The metal oxide stretching frequency seems to be more sensitive to the group to which iron is bonded. A 1% increase is observed going from HFeOH to $CH_3FeOH$ compared to a 1.8% increase in going from $CH_3FeOH$ to $C_2H_3FeOH$. In the case of the iron–carbon stretching frequency the effect is even more

**Table IV.** Comparison of Some FTIR Frequencies (cm$^{-1}$) of Bis(ethylene) Iron, Ethylene Diiron, Bis(ethylene) Diiron, Ethylene Iron Monoxide, and Nitrogen Iron Monoxide $\pi$-Complexes in Solid Argon[a]

| vib mode | Fe($C_2H_4$)$_2$ | $Fe_2$($C_2H_4$)[b] | $Fe_2$($C_2H_4$)$_2$[b] | FeO($C_2H_4$) | FeO($N_2$) |
|---|---|---|---|---|---|
| C=C stretch | 1491.2 | 1472.9 | 1466.1 | 1480.3 | |
| | | 1463.5 | 1457.7 | | |
| $CH_2$ scissor | 1221.4 | 1192.5 | 1187.5 | 1190.6 | |
| | | 1182.9 | 1171.5 | | |
| Fe=O stretch | | | | 862.7 | 887.3 |
| **vib mode** | **Fe($C_2D_4$)$_2$** | **$Fe_2$($C_2D_4$)** | **$Fe_2$($C_2D_4$)$_2$** | **FeO($C_2D_4$)** | **FeO($N_2$)** |
| C=C stretch | 1334.7 | 1303.6 | 1295.4 | 1297.4 | |
| | | 1291.8 | 1279.1 | | |
| $CH_2$ scissor | 944.0 | | 936.0 | 938.2 | |
| | | 933.1 | 924.6 | | |
| Fe=O stretch | | | | 864.2 | 887.3 |

[a] Reference 9 for Fe/$C_2H_4$ $\pi$-complexes and ref 10 for FeO($N_2$) $\pi$-complex. [b] Note that two sets of frequencies are listed for the two geometrical isomers observed for $Fe_2$($C_2H_4$) and $Fe_2$($C_2H_4$)$_2$, respectively.

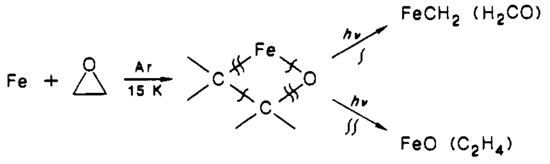
**Table V.** Comparison of Some FTIR Frequencies (cm$^{-1}$) of Vinyliron Hydride, Vinyliron Hydroxide, Methyliron Hydroxide, and Hydridoiron Hydroxide in Argon Matrices[e]

| approx type of vib mode | $H_3C_2FeH$[a] | $H_3C_2FeOH$ | $H_3CFeOH$[b] | HFeOH[c] |
|---|---|---|---|---|
| O—H stretch | | 3744.6 | 3744.8 | 3741.5 |
| | | *3749.7*[e] | | |
| C—H stretch | 2923.1 | 2917.1 | | |
| C=C stretch | 1556.3 | 1556.3 | | |
| $CH_2$ rock | 1019.0 | 1019.0 | | |
| $CH_2$ wag | 944.2 | *944.2*[e] | | |
| | | 946.4 | | |
| | | 948.1 | | |
| Fe—O stretch | | 691.1 | 687.5 | 679.8 |
| | | 693.3 | | |
| | | 696.4 | | |
| | | *699.6*[e] | | |
| Fe—C stretch | 507.2 | 541.7 | 519.5 (528.7)[d] | |
| **approx type of vib mode** | **$D_3C_2FeD$** | **$D_3C_2FeOD$** | **$D_3CFeOD$** | **DFeOD** |
| O—D stretch | | 2759.2 | 2759.6 | 2757.7 |
| | | *2762.3*[e] | | |
| C=C stretch | 1477.4 | 1480.1 | | |
| | | 1483.0 | | |
| | | *1484.9*[e] | | |
| $CD_2$ wag | 737.4 | *737.6*[e] | | |
| | | 740.5 | | |
| Fe—O stretch | | 673.8 | 667.3 | 660.5 |
| | | 677.4 | | |
| | | *681.5*[e] | | |
| Fe—C stretch | 491.0 | 527.9 | (480.2)[d] | |

[a] Reference 9. [b] Reference 11. [c] Frequencies measured in this study; for a detailed study on this molecule see ref 12. [d] $\nu_{Fe-C}$ for $H_3CFeH$, ref 13. [e] Frequencies given in italics belong to most intense peaks within the group.

pronounced where a 4% increase is measured going from $CH_3FeH$ to $C_2H_3FeH$ and a 6.8% increase is observed going from $C_2H_3FeH$ to $C_2H_3FeOH$.

**(ii) Photochemistry. (a) Metathesis Reaction.** The iron atom in its ground electronic state is shown to be capable of activating the C–O bond of ethylene oxide. A metallacycle called ferraoxetane is spontaneously formed at cryogenic temperatures in solid argon. Visible photolysis of this organometallic ring compound leads to a metathesis reaction. Two possible pathways are operative as shown below. One pathway involves the simultaneous rupture of the Fe–O and the C–C bonds. In the other mechanism it is the Fe–C and the C–O bonds that will be broken. In the first case one expects to observe the formation of formaldehyde and iron methylene whose infrared spectrum was recently measured in this laboratory.[14] In the second case iron monoxide and ethylene are expected to be formed. The observation of the ethylene iron monoxide π-complex demonstrates that metathesis of the metallacycle took place through the cleavage of the iron–carbon and carbon–oxygen bonds. A reverse modification of this metathesis reaction has been postulated in biological systems where an oxoiron porphyrin has been shown to epoxidize olefins.[1]



**(b) C–H Bond Activation of Ethylene.** The ultraviolet photolysis of $FeO(C_2H_4)$ resulted in its photorearrangement through the activation of one of the C–H bonds of ethylene. Iron monoxide photoinserted into one of the C–H bonds and formed vinyliron hydroxide. The carbon–hydrogen bond activation of ethylene has been recently observed by Kafafi et al.[9] via the photoexcitation of a different reaction intermediate, namely, an ethylene iron hydrogen-bonded complex. In the studies of the cryochemistry of iron and ethylene, Kafafi et al.[9] showed that the photoexcitation of the hydrogen-bonded complex leads to C–H activation whereas photoexcitation of the π-complexes $Fe(C_2H_4)_2$, $Fe_2(C_2H_4)$, and $Fe_2(C_2H_4)_2$ resulted in some cases in their isomerization and eventually led to their dissociation. Recent experimental studies on the iron/cyclopropane photochemistry in cryogenic matrices have shown that an ethylene–iron methylene π-complex is formed as an intermediate.[15] This π-complex photorearranged upon UV excitation and formed a methyl vinyliron or a vinyliron methide, thus indicating insertion of the iron methylene into one of the C–H bonds of ethylene. This mechanism is thus very similar to the one deduced from the present study. This result is not surprising since FeO and $FeCH_2$ are isovalent and are expected to react in a similar fashion. Figure 4 summarizes the iron/ethylene oxide photochemistry that has taken place in solid argon.

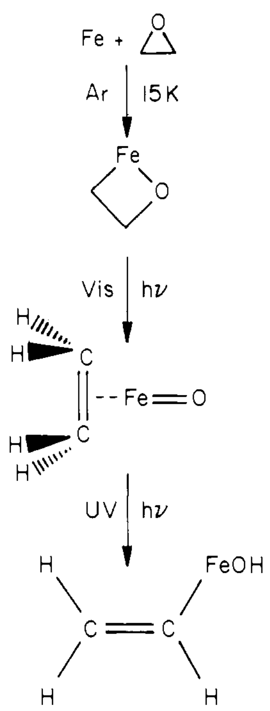
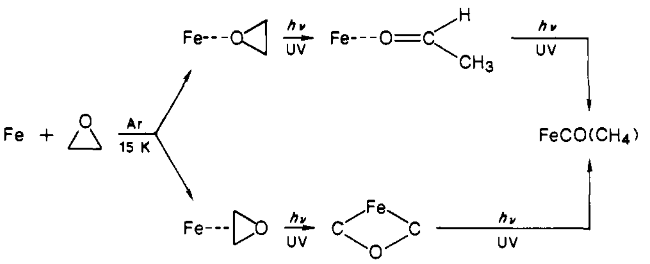


**Figure 4.** Iron/ethylene oxide photochemistry in solid argon.

**(c) The Photofragmentation of Ethylene Oxide.** Evidence from peaks observed in the C≡O stretching region as well as methane peaks in some experiments suggests the presence of a secondary reaction pathway for the monoiron/ethylene oxide photochemistry leading to the almost complete fragmentation of ethylene oxide. One may speculate about possible mechanisms that will result in carbon monoxide formation. One of them will involve the C–C bond activation of ethylene oxide followed by elimination of methane. The other mechanism will lead to the formation of an acetaldehyde iron complex again followed by the photodisproportionation to $FeCO(CH_4)$. Evidence for these two reaction pathways has been previously observed for the gas-phase reactions



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(14) Chang, Sou-Chan; Kafafi, Zakya H.; Hauge, Robert H.; Billups, W. Edward; Margrave, John L. *J. Am. Chem. Soc.* **1985**, *107*, 1447.

(15) Kafafi, Zakya H.; Hauge, Robert H.; Billups, W. Edward; Margrave, John L., to be published.

of the cations $Fe^+$, $Co^+$, and $Ni^+$ with ethylene oxide.[16,17] Previous matrix isolation studies on the chemistry of $Fe/CH_3OH$ have shown that photoactivation of the $Fe(CH_3OH)$ adduct in the violet and ultraviolet regions led to the metal atom insertion into the O–H and C–O bonds of methanol, respectively. Photofragmentation of methanol occurred via UV excitation of its O–H insertion reaction intermediate, namely methoxyiron hydride, $CH_3OFeH$.[11] Peaks associated with CO, FeCO, and $FeH_2$ were observed, which suggested the photofragmentation of methanol to carbon monoxide and hydrogen.

## V. Concluding Remarks

1. The infrared spectrum of the first and one of the simplest oxametallacycles, ferraoxetane, was obtained from the spontaneous insertion of an iron atom into the C–O bond of ethylene oxide in solid argon at 12.5–15 K.

2. Upon broad band irradiation with visible light, a metathesis reaction was observed with simultaneous cleavage of the C–O and Fe–C bonds of the oxametallacycle. The photoproduct was an iron monoxide molecule interacting with an ethylene molecule through the $\pi$-system. The FTIR spectrum of this $\pi$-complex was measured and compared to similar $\pi$-complexes.

3. The C–H activation of one of the inert C–H bonds of ethylene was achieved by UV photolysis of $FeO(C_2H_4)$. The FTIR spectrum of vinyliron hydroxide was thus identified for the first time.

4. Diiron seemed to have undergone similar photochemistry although a more detailed study is needed to confirm the reaction mechanism.

5. Evidence from the observation of an FeOFe stretching frequency suggests the formation of a double insertion product, a five-membered ring where the two iron atoms are bridging the oxygen atom, at one end and bonded to ethylene at the other end.

6. A secondary reaction for the metal atom appeared to have taken place leading to the photofragmentation of ethylene oxide into methane and carbon monoxide. More work is needed to delineate the mechanism of this reaction. A similar reaction was also observed for diiron where the final product was identified as a perturbed diiron monocarbonyl.

**Acknowledgment.** The authors acknowledge financial support from the National Science Foundation, the Robert A. Welch Foundation, and 3M Co. The help of Suzanne Gibbs Robins in running preliminary experiments on the Beckman IR-9 and John Venier in plotting spectra presented in this paper is greatly appreciated.

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(16) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1829.

(17) Beauchamp, J. L., private communication.

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# Circular Dichroism Studies of the Solution Structure of Chiral Pyridine Substituted Crowns and Their Complexes

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**Abstract:** The solution structures of a series of chiral pyridino-18-crown-6 macrocycles and their alkali and alkaline earth complexes have been studied with circular dichroism (CD) spectroscopy. The crowns (4*S*,14*S*)-4,14-dimethyl-2,16-dithioxopyridino-18-crown-6, its 2,16-dioxo analogue, its 2,16-tetrahydro analogue, and (5*S*,13*S*)-5,13-diphenyl-2,16-dioxopyridino-18-crown-6 contain pyridine chromophores that have been used as direct structural probes. The induced CD in the lowest energy $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of pyridine has been interpreted in terms of the one-electron theory of optical activity. Sector rules have been derived for each of these transitions and used to predict the structures of these crowns and their complexes. These predictions are consistent with the results obtained from $^1H$ NMR spectroscopy.

The structures of crystalline macrocyclic polyethers and their complexes have been widely studied by means of X-ray diffraction.[1] In the solid state, lattice forces, including the accommodation of the anion, may significantly influence the crown complex structure. On the other hand, in dilute solution, solvation of the anion and the crown complex, as well as ion pairing, is the important structural influence. Since the ionophoric properties of crown ethers in solution are of such significance, it is important to study their solution structures directly. However, only a limited number of studies have addressed the question of crown conformation and anion coordination in solution. These include the use of IR,[2] NMR,[3] and UV[4] spectroscopies to determine the conformations of free and complexed crowns[2,3] and to measure complex formation.[4] UV spectra have also been used to probe the structure of crown complexed fluorenyl ion pairs in solution.[5]

The introduction of a chiral center (or centers) into the crown macrocycle opens the possibility of using circular dichroism (CD) spectroscopy as an additional structural probe. The well-established sensitivity of CD to conformational changes can provide more information than simple absorption spectra. CD has been used, for example, to study the solution structures of chiral dimethyl substituted benzo-15-crown-5 ethers and their complexes[6] and of chiral methyl substituted 18-crown-6 ether complexes of alkali and alkaline earth nitrate ion pairs.[7] In the work reported

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(1) For several excellent reviews, see: (a) Dobler, M. *Ionophores and Their Structures*; John Wiley and Sons: New York, 1981; Chapter 8. (b) Dobler, M. *Chimia* **1984**, *38*, 415. (c) Truter, M. R. *Struct. Bonding* (*Berlin*) **1973**, *16*, 71.

(2) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1972**, *26*, 1471.

(3) (a) Dale, J. *Isr. J. Chem.* **1980**, *20*, 3. (b) Lockhart, J. C.; Robson, A. C.; Thompson, M. E.; Tyson, P. D.; Wallace, I. H. M. *J. Chem. Soc., Dalton Trans.* **1978**, 611.

(4) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(5) Wong, K. H.; Konizer, G.; Smid, J. *J. Am. Chem. Soc.* **1970**, *92*, 666.

(6) (a) Mack, M. P.; Hendrixson, R. R.; Palmer, R. A.; Ghirardelli, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7830. (b) Mack, M. P.; Hendrixson, R. R.; Palmer, R. A.; Ghirardelli, R. G. *J. Org. Chem.* **1983**, *48*, 2029.

0002-7863/87/1509-4780$01.50/0