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Matrix Isolation Infrared and Mössbauer Studies of the Oxidative Addition Reactions of the Hydrogen Halides with Iron Atoms[1]

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Abstract: The reactions of the hydrogen halides with iron atoms in inert matrices lead to the previously unknown molecules H-Fe-X (X = Cl, Br, I). Infrared studies with Ar/Fe/HX (5%) and Kr/Fe/HX (5%) show one new band in the region 1735-1755 cm^{-1}. This is assigned to the iron-hydride stretch of H-Fe-X. Mössbauer studies of Ar/Fe/HX (5%) show the formation of one major product in each case. These products all have isomer shifts characteristic of Fe(II) complexes, hence they are similarly assigned to the oxidative addition product H-Fe-X. Mössbauer studies using Ar/Fe/HF show different behavior. At 6 K, two products are observed. These are assigned to an Fe(FH) complex, and to matrix isolated FeF_2. Warming this sample to 77 K causes loss of the matrix, leaving amorphous FeF_2 and FeF_3.

One of the fundamental reactions of organometallic chemistry is oxidative addition of a metal across a bond of a reactant. This reaction is a key step in several homogeneous industrial processes.[2] Examples of this are the oxidative addition of CH_3I by a rhodium complex in the Monsanto process for the manufacture of acetic acid from methanol and the oxidative addition of water by a palladium complex in the Wacker process for the manufacture of acetaldehyde from ethylene.

These syntheses are all carried out in donor solvents, thus the nature of the active species is not always obvious. In addition to possible solvent effects, there are the other ligands that remain attached to the metal atom during the reaction. This means that there are always additional steric and electronic effects present. Even model systems such as Vaska's compound have the same limitations. This makes understanding the role of the metal atom more difficult to define.

An ideal model system for studying the effects of both the metal center and the ligands would be a single metal atom, a simple molecule AB which will undergo oxidative addition, and the absence of solvent. Matrix isolation allows the study of single metal atoms with a reactant diluted in a noble gas.[3] This closely approximates the ideal solvent free conditions. For these reasons we have chosen to investigate the reactions of iron atoms with the hydrogen halides. To our knowledge, this paper offers the first example of oxidative addition reactions of iron atoms under matrix isolation conditions that do not require photolysis for product formation.

Experimental

Detailed descriptions of both the Mössbauer[4] and the infrared[5] vacuum systems have been published.

In brief, infrared samples are prepared on a NaCl substrate held at 16-20 K by an Air Products Model CSA-202 Closed Cycle Helium Refrigerator (Displex) by codeposition of iron vapor with the matrix and reactive gases which have been premixed. Infrared spectra were recorded either on a noncommercial spectrometer which has been described previously[6] or with a Perkin-Elmer 683.

Mössbauer samples are prepared on a Be substrate attached either to the end of a Janis DT liquid helium cryostat or to the cold finger of a modified Air Products Model 202.[5] Spectra are obtained with a conventional constant acceleration spectrometer using a ^{57}Co in Rh source and are computer fit with a least-squares routine to a sum of quadrupole doublets with Lorentzian line shapes. The pairs of peaks were constrained to have equal amplitudes and widths. The standard statistical tests, X^2 and MISFIT, were used as quantitative measures of the quality of the fits. Isomer shifts are reported relative to α-Fe metal at room temperature.

Gaseous iron atoms were formed either by evaporating iron powder (99.99% natural abundance Fe from Research Chemical Corp. for infrared and 95.85% enriched ^{57}Fe from New England Nuclear for Mössbauer) from an alumina crucible or by direct resistive heating of an iron foil[7] (99.99% from Materials Research Corp.). Kr (99.995%), Ar (99.999%), HI (98%), HBr (99.8%), and HCl (99%) supplied by Linde and the HF (99.9%) from Matheson were used without further purification. DCl (99%) was from KOR Isotopes.

Photolysis studies were carried out with a 400-W high-pressure Xenon lamp as a source. The unfiltered arc of the lamp was focused onto the substrate through a quartz window in the vacuum system.

Results

The infrared spectra obtained when iron vapor (evaporated at various temperatures) is codeposited with an Ar/HI (5%) gas mixture are shown in Figure 1. The constant background bands are due to traces of atmospheric water in the IR source box and not present in the matrix. The prominent feature at 1754 cm^{-1} increases in size as the iron concentration in the sample is increased. The similarity in the position of this peak to the iron-hydride stretching frequencies found for the molecules H-Fe-OH (1732 cm^{-1})[8] and H-Fe-NH_2 (1717 cm^{-1})[9] suggests an assignment of the band to the Fe-H stretch of the oxidative addition product, H-Fe-I.

The iron stoichiometry of the product can be confirmed by plotting the log of the intensity of the absorption vs. the log of the iron concentration[6] as shown in Figure 2. The slope of the straight line (0.82) being very close to one is good evidence that the product contains a single iron atom.

The Mössbauer spectrum obtained from a similar sample consists principally of one quadrupole doublet due to the a single iron reaction product C (Figure 3). The isomer shift (δ = +0.60 mm/s) is in the region where ionic Fe(II) molecules absorb, providing further evidence for the assignment given above.

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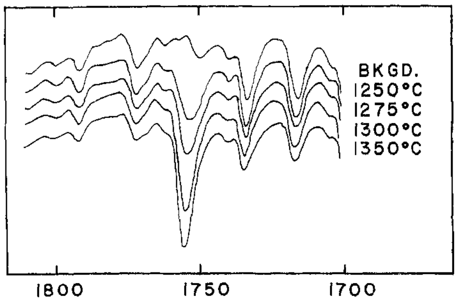

Figure 1. A portion of the infrared spectra of Ar/HI (5%) matrices containing iron deposited at various furnace temperatures. Absorptions which remain approximately constant in the spectra are due to atmospheric water. (BKGD is a background spectrum with no iron in the matrix).

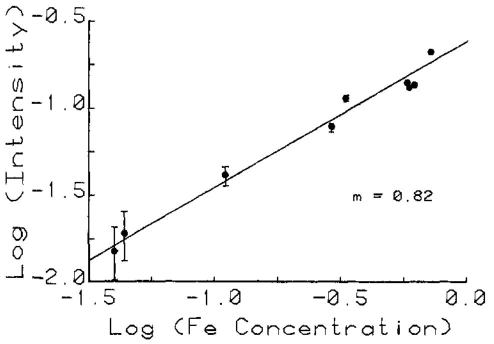

Figure 2. Plot of the log of the intensity of the 1754-cm^{-1} absorption in Figure 1 vs. the log of the iron concentration.

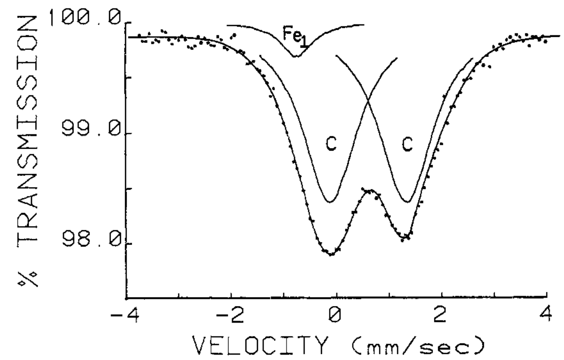

Figure 3. ^{57}Fe Mšsbauer spectrum of iron (0.9%) in an Ar/HI (5%) matrix, deposited at ~15 K. The peak labeled Fe$_1$ may be due to small amounts of unreacted iron atoms (see text).

Similar spectra were obtained for both HBr and HCl samples. HCl gave a band at 1755 cm^{-1} in an argon matrix and a 1739 cm^{-1} band in krypton. In addition, a 1:1 mixture of HCl and DCl in krypton gave bands at 1740 and at 1245 cm^{-1}, with no bands in between. This experiment confirms the nature of the bands and also the assumption that only one molecule of HX reacts with one Fe. The Mössbauer spectrum of an Ar/HCl (5%) matrix at 4 K containing 0.68% iron is shown in Figure 4a. In addition to the absorption due to the oxidative addition product H–Fe–Cl (labeled A in the figure), a quadrupole doublet with an isomer shift identical with that of unreacted iron monomers in rare gases is presented (Fe$_1$). The quadrupole splitting (Δ) of the monomer in this matrix is caused by the neighboring HCl molecules which produce a noncubic site symmetry around the iron atoms. In rare gas matrices which have cubic symmetry, a single broad peak is observed.[10] For HBr- and HI- containing matrices, it is possible that there were small amounts (~5%) of unreacted iron atoms producing an unsplit Mössbauer absorption at $\delta = -0.75$ mm/s. The lack of quadrupole splitting could indicate that the iron atoms in these matrices are surrounded by only Ar atoms. The absorption from these iron monomers lead to an asymmetry in the absorption for H–Fe–X (X = Br, I) as shown in Figure 3. However, this small asymmetry could also be explained by a small net degree of orientation, for example, if more molecules lay in the plane of the Be disk than were perpendicular to it. Such orientation effects have been previously noted for Fe$_2$[11] and CuF$_2$.[12] The available data do not permit us to make a definitive choice between these two hypotheses. Further, it appears difficult to reconcile the absence of this asymmetry in the matrices containing a similar

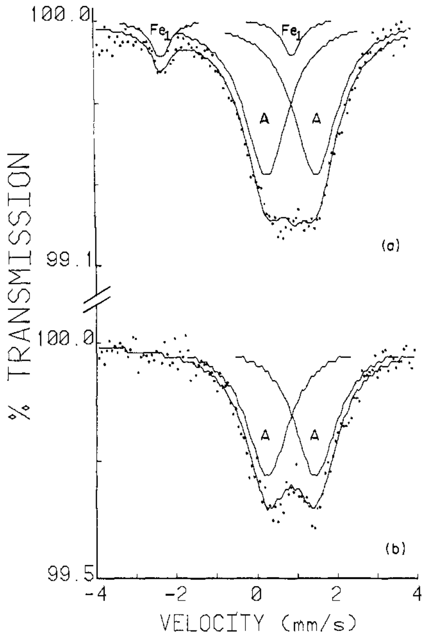

Figure 4. The 6 K Mössbauer spectrum of an Fe (0.68%)/Ar/HCl (5%) matrix (a) as deposited and (b) after 12 min of irradiation with the unfiltered arc of a high-pressure Xenon lamp.

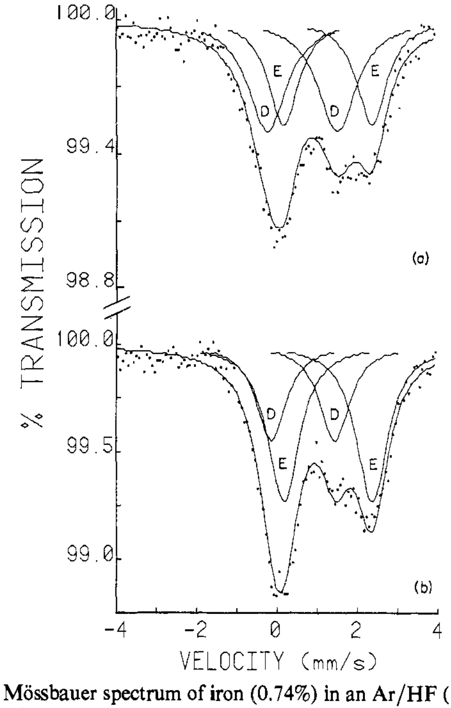

Figure 5. Mössbauer spectrum of iron (0.74%) in an Ar/HF (7%) matrix taken (a) after deposition at ~6 K and (b) after 15 min of unfiltered irradiation.

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Table I. Mossbauer Parameters[a,b] of the Species Observed in the Iron-Hydrogen Halide Reactions

species	matrix	T, K	δ	Δ	Γ	assignment
Fe_1	Ar/HCl (5%)	6	−0.73	3.25	0.59	Fe_1
A	Ar/HCl (5%)	6	+0.87	1.22	1.33	H-Fe-Cl
B	Ar/HBr (5%)	6	+0.92	1.28	1.37	H-Fe-Br
C	Ar/HI (5%)	15	+0.60	1.45	1.24	H-Fe-I
D	Ar/HF (7%)	6	+0.63	1.74	1.00	Fe (FH)
E	Ar/HF (7%)	6	+1.26	2.20	0.91	FeF_2
F	none	77	+1.35	2.91	0.60	amorphous FeF_2
		300	+1.23	2.52	0.71	
G	none	77	+0.45	0.60	0.73	amorphous FeF_3
		300	+0.53	0.48	0.57	

[a] Isomer shift (δ), quadrupole splitting (Δ), and line width (Γ) are in mm/s and are all ±0.06 mm/s. [b] Isomer shifts are given with respect to iron metal at room temperature.

concentration of HCl. We also recognize that other explanations of the asymmetry are possible.

The unreacted iron atoms in HCl-containing matrices can be converted to the product, H-Fe-Cl, by irradiation of the sample with the unfiltered arc of a high-pressure xenon lamp (Figure 4b). Considerable heating is observed during this irradiation due to the source output in the visible and infrared. This conversion is reminiscent of the behavior of unreacted iron atoms in pure CO[5] and C_2H_4[7] matrices on irradiation.

The behavior of HF toward iron atoms differs significantly from that of the other hydrogen halides. Infrared studies by Kauffman indicate that an Fe(FH) complex is initially formed on deposition, and photolysis with 300–340-nm light is required to form the oxidative addition product, H–Fe–F.[9] This information is helpful in understanding the Mössbauer spectrum of an Ar/HF (5%) matrix containing 0.74% iron shown in Figure 5a. The parameters for the peaks labeled D in the spectrum (see Table I) are different from those of the H–Fe–X (X = Cl, Br, I) molecules. They are also very different from those that might be expected for the ionic product H–Fe–F. On the basis of the electronegativity of the halide, the isomer shift would be expected to be at least as positive as those of the chloride and bromide complexes, and probably more positive.[13] However, the isomer shift of D is very similar to that of the $Fe(C_2H_4)$[7] and $Fe(NH_3)$[14] molecules, hence we assign this product to Fe(FH).

In contrast to the infrared studies of Kaufman, we find an additional quadruupole doublet (E) in this spectrum with parameters that indicate a product quite different from the Fe(FH) complex. Further, product E grows at the expense of the complex D when the sample is irradiated with the unfiltered UV source (Figure 5b). The isomer shift of product E ($\delta = +1.26$ mm/s) is in the region where highly ionic Fe^{2+} compounds absorb. Thus, we identify the peaks E as arising from FeF_2 molecules which are surrounded by Ar and/or HF neighbors. These peaks have rather broad line widths (∼1.0 mm/s) suggesting that some variance in the electric field gradient (EFG) at the iron nucleus and hence of the quadrupole splitting is present for the products. This variance could be due to a differing number of Ar and HF nearest neighbors for the products in this matrix, causing a range of quadrupole splittings for these species. The superposition of the spectra for these products will produce broadened lines.

The presence of FeF_2 in our samples can be explained by the higher concentration of HF in the gas mixtures used for our Mössbauer experiments (7%) relative to the infrared studies (≤1%) of Kauffman. Further, HF is known to aggregate in the gas phase at room temperature.[15] Thus, higher concentrations of dimeric and polymeric HF aggregates would be present in our Mössbauer samples.

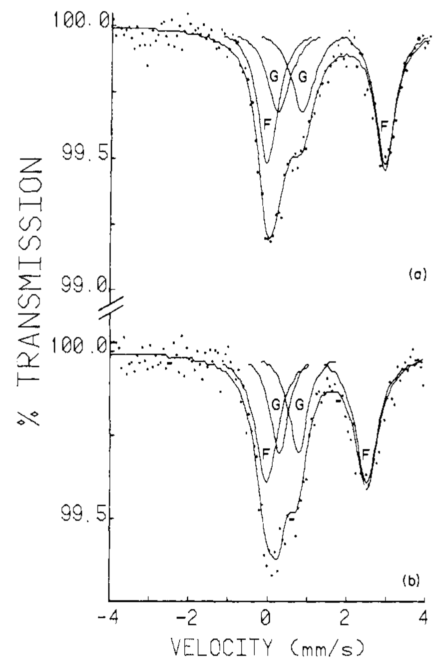

Figure 6. Mössbauer spectrum of the sample in Figure 5 taken after warming to (a) 77 K where the matrix evaporates and (b) 300 K.

Table II. ν_{Fe-H} Frequencies (±1 cm⁻¹) for the H-Fe-X (X = F, Cl, Br, I) Species in Argon and Krypton Matrices

	ν_{Fe-H}, cm^{-1}	
species	Ar	Kr
H-Fe-F[a]	1752	
H-Fe-Cl	1755	1739
H-Fe-Br		1738
H-Fe-I	1754	

[a] Reference 10.

Evidence that this higher concentration of aggregates could be responsible for the production of FeF_2 can be found in studies of various concentrations of HI in matrices.[16] At very low concentrations (1% HI xenon) such that Fe/HI nearest neighbors are minimized, only unreacted iron atoms are produced. As the HI concentration is increased and iron and HI molecules come in contact in the matrix, the oxidative addition product. H–Fe–I, is formed. When iron atoms find themselves next to more than one HI molecule (15–100% HI in xenon), FeI_2 and small amounts of FeI_3 are formed.

The identification of FeF_2 upon deposition in our experiments is further supported by the spectra obtained when the sample is warmed to 77 K where the matrix evaporates (Figure 6a), and 300 K (Figure 6b). The peaks labeled F and G in the Figures can be assigned to amorphous FeF_2 and FeF_3, respectively. Literature values for amorphous FeF_2[17] are Δ ∼2.7 at 77 K and Δ ∼2.4 at 300 K (δ was not given) and for amorphous FeF_3[18] they are $\delta = +0.45$ and $\Delta = 0.55$ at 300 K. In view of the very different methods of preparation, the agreement with the literature parameters is satisfactory.

The Mössbauer parameters for all species discussed are gathered together in Table I and the infrared data for the H–Fe–X species are given in Table II.

Discussion

The reaction of iron atoms with the hydrogen halides under matrix isolation conditions leads to the previously unknown

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molecules H–Fe–X (X = Cl, Br, I). This reaction proceed directly to the product in the case of X = Cl, Br, and I; however, for X = F, photolysis of an intermediate complex, Fe(FH), is required.[9]

The observation of the oxidative addition products H–Fe–X (X = Cl, Br, I) by direct reaction is the most striking feature of this study. The observation of Fe(FH) implies that the mechanism of the reaction is the following

$$\mathrm{Fe + HX \rightarrow Fe(XH) \rightarrow H{-}Fe{-}X} \qquad (1)$$

For X = Cl, Br, and I the intermediate complex is too unstable to isolate even under conditions of extreme dilution. Instead, the complex reacts further to give the oxidative addition product H–Fe–X. In the case of X = F the activation energy for this step must be greater than the available thermal energy and so the reaction stops at the intermediate. Unfortunately, for both the thermal and photolytic reactions we are unable say whether the addition is concerted or involves sequential addition of either H or X followed by addition of the second reactant. In any event, concerted addition is energetically more favorable. If the mechanism is sequential addition, then the absence of Fe–H (and of Fe–F for X = F) requires that the second reactant cannot escape from the intermediate formed by the first addition.

Two possible explanations of the difference in reactivity of HF relative to HCl, HBr, and HI are the differences in the bond energies and the differences in the acidities of the hydrogen halides. The trend in the bond energies is HF > HCl > HI and that in the gas phase acid strengths is HI > HBr > HCl > HF. If these data are considered with those of CH_4,[19,20] NH_3,[9,14] and H_2O,[8] then it is possible to decide between the two possibilities. The bond energies of CH_4, NH_3, H_2O, and HCl are all ~100 kcal/mol, yet the first three undergo oxidative addition with iron atoms only on irradiation. Thus, the available data suggest that the acidity of the reactant molecule is the crucial factor as to whether or not the molecule will undergo oxidative addition with iron atoms without the necessity of radiation. By acidity we mean the ease with which dissociation into H^+ and X^- can occur, as induced by the Fe atom. Other possible explanations also exist. Methane may be too sterically crowded. Ammonia, water, and HF may form a σ donor bond that is too strong and unfavorably oriented for oxidative addition.

There are two possible structures for H–Fe–X, linear ($C_{\infty v}$) and bent (C_s). (The possibility of a cyclic structure can be eliminated by the observation of a terminal Fe–H vibration). The isoelectronic molecules FeF_2 and $FeCl_2$ have been shown to be linear,[21,22] although a recent study[23] concluded that $FeCl_2$ was slightly bent with a bond angle of 160°. On this basis, it is concluded that the H–Fe–X species are linear or nearly so.

From Table II it is apparent that in the H–Fe–X complexes, the position of $\nu_{\mathrm{Fe-H}}$ is independent of the nature of X. the value of ~1750 cm^{-1} is appreciably higher than that of diatomic Fe–H[24] (1661 cm^{-1} in argon). If it is assumed that the anharmonicity correction is similar for the $\nu_{\mathrm{Fe-H}}$ vibration in both Fe–H and H–Fe–X, then the higher frequency is indicative of a stronger Fe–H bond in H–Fe–X than in Fe–H. This is reasonable because the metal center is formally Fe^{2+} in H–Fe–X vs. Fe^+ in Fe–H. This interpretation is supported by the Mössbauer parameters of the H–Fe–X molecules. The isomer shifts are in the range expected for ionic Fe(II) complexes (+0.5 to +1.0 mm/s). The order of the isomer shifts in H–Fe–X, X = C ≈ Br > I (the difference in the isomer shifts for X = Cl, Br is not significant), is consistent with this. Matrix-isolated $FeCl_2$ and $FeBr_2$ have approximately the same isomer shift (+0.88 and +0.81 mm/s, respectively),[25] implying a similar degree of ionicity for Cl^- and Br^- as found here. The less positive isomer shift of H–Fe–I can be rationalized by noting that the more polarizable and less electronegative I^- ion will engage in more covalent bonding than will the other halides.

Although the value of the $\nu_{\mathrm{Fe-H}}$ vibration in H–Fe–R is independent of the nature of R, for R = halide, this is not the usual case. As the periodic table is traversed there is a very interesting trend in $\nu_{\mathrm{Fe-H}}$:

	$H{-}Fe{-}CH_3$	$H{-}Fe{-}NH_2$	H–Fe–OH	H–Fe–Hal
$\nu_{\mathrm{Fe-H}}$ (cm^{-1})	1684	1717	1732	~1750

This trend is in agreement with the expected increasingly ionic nature of the bonding in these complexes.

A theoretical investigation[26] of molecular complexes of a neutral lithium atom with the dipolar molecules NH_3, H_2O, HF, PH_3, H_2S, and HCl (ZH_n) concluded that the minimum energy structure was Li–ZH_n, where the negatively charged Z approaches the metal atom. Charge transfer from ZH_n causes a weakening of the Z–H bond(s) and hence a decrease in the corresponding stretching frequency. For NH_3, H_2O, and HF the most stable structure has the Li–Z vector and the dipole vector of ZH_n collinear. As is discussed more fully in ref 5 and 7, the isomer shift of Fe(FH) is consistent with an electronic configuration of [Ar] $(3d)^7(4s)^1$ with little or no $d_\pi \rightarrow \pi^*$ back-bonding. The effect of the rehybridization of the iron atom from $(3d)^6(4s)^2$ to $(3d)^7(4s)^1$ is that the highest occupied orbital is now a semifilled s orbital exactly as in Li. Thus the bonding should be analgous to that of the (hypothetical) complex, Li(FH). HF has no low-lying π^* orbitals so $d_\pi \rightarrow \pi^*$ would not be expected to occur. Hence, by analogy to the theoretical study, Fe(FH) is formulated as a linear F-bonded complex. The Mössbauer parameters of Fe(FH) (Table I) are in complete agreement with this. The reason for the similarity of the isomer shifts of $Fe(NH_3)$ and Fe(FH) is now apparent; the bonding in the two complexes is virtually identical.

In addition to an activation energy for the process Fe(XH) → H–Fe–X there must also be a sizable activation energy for the formation of Fe(XH). This is suggested by the presence of unreacted iron atoms in HCl containing matrices. The quadrupole splitting present for these iron atoms implies that one or more HCl molecules are close enough (probably as part of the matrix cage) to cause the quadrupole splitting. However, even at this close proximity, there is insufficient energy to form the Fe(ClH) complex.

The rehybridization of the iron atom possibly explains the existence of the activation energy for the formation of Fe(XH). In the gas phase[27] the energy differences between the ground state ($^5D_5$) and lowest state of the $(3d)^7(4s)^1$ multiplet ($^5F_5$) is 6928 cm^{-1}. Even if the matrix environment reduces this difference somewhat (as seems probable),[28] there will still be a sizable activation energy. This would seem to imply that the complex is fairly strongly bonded in order to provide the thermodynamic driving force for its formation.

Finally, the formation of FeF_2 without the intermediacy of H–Fe–F implies that its formation requires a simultaneous reaction of at least three molecules

$$\mathrm{Fe + 2HF \ or\ (HF)_{n>1} \rightarrow FeF_2} \qquad (2)$$

rather than a sequential reaction:

$$\mathrm{Fe \xrightarrow{HF} H{-}Fe{-}F \xrightarrow{HF} FeF_2} \qquad (3)$$

This mechanism also explains the effect of increasing the HI concentration. At very low HI concentration isolated, unperturbed Fe atoms are obtained.[16] Raising the HI concentration results in the formation of H–Fe–I. At HI concentrations above 15%

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no trace of H–Fe–I is observed in the infrared spectrum. The Mössbauer spectrum of Fe in pure HI shows the formation of FeI_2.

From these considerations, the products obtained from the reaction of iron atoms with the hydrogen halides as a function of HX (X = F, Cl, Br, I) concentration in inert matrices can be summarized as follows:

$$Fe + HX\ (<1\%) \rightarrow Fe_1 \tag{4}$$

$$Fe + HX\ (1\text{–}10\%) \rightarrow H\text{–}Fe\text{–}X\ (X \neq F)\ \text{or}\ Fe(FH)\ (X = F) \tag{5}$$

$$Fe + HX\ (>7\%) \rightarrow FeX_2 \tag{6}$$

Thus, as the HX concentration is progressively raised, (4), then (5), then (6) becomes the predominant reaction.

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Registry No. Fe, 7439-89-6; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; HF, 7664-39-3; Ar, 7440-37-1; H-Fe-Cl, 88610-39-3; H-Fe-Br, 88610-40-6; H-Fe-I, 88610-41-7; FeF_2, 7789-28-8; FeF_3, 7783-50-8; Kr, 7439-90-9.

Mechanism of Halogenation of Dimanganese, Manganese–Rhenium, and Dirhenium Decacarbonyls

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Abstract: The reactions between halogens ($X_2 = Cl_2, Br_2, I_2$, and ICl) and $M_2(CO)_{10}$ ($M_2 = Mn_2$, MnRe, and Re_2) in CH_3CN solvent yield equal amounts of $M(CO)_5X$ and $[M(CO)_5(CH_3CN)]^+$. For $X_2 = I_2$ the rate law was shown to obey second-order kinetics, $k[M_2(CO)_{10}][I_2]$. For $M_2 = Re_2$ the activation parameters were $\Delta H^\ddagger = 5.8 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -34.9 \pm 0.9$ cal/(mol K), for M_2 = MnRe $\Delta H^\ddagger = 6.3 \pm 1.5$ kcal/mol and $\Delta S^\ddagger = -41 \pm 6$ cal/(mol K), and for $M_2 = Mn_2$ $\Delta H^\ddagger = 8.5 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -39 \pm 5$ cal/(mol K). The relative rates of halogenation follow the order $Re_2(CO)_{10} > MnRe(CO)_{10} > Mn_2(CO)_{10}$, which opposes the order expected based upon homolysis of the metal–metal bond. The rate of iodination varies by more than a millionfold depending on the solvent. In nonpolar solvents such as decalin or toluene the oxidation proceeds slowly to yield $M(CO)_5I$, whereas in CH_3CN or CH_3NO_2 the reaction proceeds rapidly to produce both $M(CO)_5I$ and $[M(CO)_5(solvent)]^+$. The evidence suggests that halogen attacks the metal–metal bond via one end of the dihalogen molecule and that heterolytic cleavage of the halogen–halogen bond takes place to yield free halide ion and a halogenium-bridged metal dimer. In many respects this resembles the mechanism for the bromination of alkenes.

The reaction between metal–metal bonded carbonyls and halogens frequently yields monomeric metal carbonyl halides.[1] For example, the standard preparation of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) proceeds from the action of X_2 on $M_2(CO)_{10}$.[2-7] Few mechanistic studies concerning this reaction type have been reported. Haines, Hopgood, and Poë described[8] the reaction between iodine and $Mn_2(CO)_{10}$ according to the rate law $k_1[Mn_2(CO)_{10}] + k_2[Mn_2(CO)_{10}][I_2]$. Here k_1 is a first-order rate constant similar to the rate of decomposition in an oxygenated solvent at the same temperature, and the second term results from a bimolecular reaction between I_2 and $Mn_2(CO)_{10}$. A similar rate law was obtained[9a] with $Re_2(CO)_{10}$ and I_2; however, the activation parameters differ greatly from those of $Mn_2(CO)_{10}$. The two iodination reactions were postulated[9a] to proceed by different mechanisms.

Candlin and Cooper[10] reported formation of a cluster–halogen charge-transfer complex in the reaction between $Os_3(CO)_{12}$ and Cl_2 or Br_2. The ultimate product is the linear molecule $[X\{Os(CO)_3\}_3X]$. A series of product studies for halogenation of $[\{M'(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$[11-14] (M′ = Fe or Ru) and $[\{M(\eta^5\text{-}C_5H_5)(CO)_2L\}]$ (M = Mo or W, L = CO; M = Mo, L = $P(OCH_3)_3$)[15,16] have suggested that these reactions proceed via a halogen-bridged intermediate. The general mechanism that was proposed involves initial electrophilic attack of the dihalogen molecule on the metal complex, followed by heterolytic cleavage of the halogen–halogen bond and formation of a halide-bridged cationic intermediate. This intermediate, which could be isolated in certain instances, then undergoes nucleophilic attack by the halide ion to afford the neutral halide complex. No kinetic studies were reported in support of this mechanism.

In other kinetic studies, Cullen and Hou[17] proposed a bimolecular pathway for the reaction of iodine and some $[M_2(CO)_8$-

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