Matrix Isolation of Electron Bombarded Gases Containing $Fe(CO)_5$: An FTIR Absorption Study of Neutral and Anion Decomposition Products

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$Fe(CO)_5$ was used as a probe of the efficiency of cation and anion trapping in cryogenic matrices under electron-bombardment, matrix-isolation spectroscopy (EBMIS) conditions. Ar gas containing $Fe(CO)_5$ (1:1000−3000; Fe:Ar) was subjected to electron bombardment with 150−300 eV electrons above a 16 K spectroscopic window. FTIR spectroscopic analysis of the matrix-isolated products demonstrates the presence of the known neutral and anionic subcarbonyl species, $Fe(CO)_n$ ($n = 2$, 3, and 4) and $Fe(CO)_m^-$ ($m = 3$ and 4). Yields for both neutrals and anions diminish significantly with decreasing carbonyl ligand number. Annealing studies in Ar indicate facile conversion of $Fe(CO)_4$ and $Fe(CO)_4^-$ to higher nuclearity iron polycarbonyls, including $Fe_2(CO)_9$. Irradiation with visible light of samples of electron bombarded $Fe(CO)_5$ in Ar was found to stimulate loss of $Fe(CO)_4$ to form $Fe(CO)_5$ by photoinduced CO recombination. Further irradiation with UV−visible light resulted in additional loss of $Fe(CO)_5$ and $Fe(CO)_4^-$, and loss of features attributed to CO perturbed by $Fe(CO)_4^-$, with concomitant production of $Fe(CO)_4$. The mechanism for formation of these products and the efficiency of ion trapping was further investigated through electron bombardment of $Fe(CO)_5$ in Ar containing small amounts of CH_4 or N_2, and in pure Kr, Xe, CH_4, and N_2. Essentially the same distribution of neutral and anionic products was observed in Kr and Xe, but with somewhat diminishing yields. The presence of small amounts of CH_4 (4%) or N_2 (2%) in Ar resulted in decreased yields of all products (<50%), with preferential loss of features associated with $Fe(CO)_4$ compared with $Fe(CO)_4^-$. Experiments in pure methane gave very small product yields (<10%), and in pure N_2, no products were observed. Anion product yields are consistent with gas-phase studies of the dissociative capture of low-energy electrons by iron pentacarbonyl, and therefore, the matrix-isolated products appear to be qualitatively representative of the gas-phase product distribution for such a process. The absence of cationic species is in contrast to the efficient production of all cationic subcarbonyls in gas-phase EI experiments. This difference is believed to be due to the low efficiency with which Ar, Kr, or Xe trap cationic species, as well as the high concentration of scattered secondary electrons in the EBMIS environment, resulting in the isolation of the neutral counterparts of cationic species.

Introduction

The spectroscopy and chemistry of ionic organometallic species is an area of current research interest. The paucity of vibrational spectroscopic data on ionic organometallic species in gas or condensed phase, relative to their neutral counterparts, demonstrates the need for an efficient and versatile approach to generation of stabilized molecular ions and their associated fragment ions. As well, there remains a need for routine techniques that complement modern mass spectrometric tools, particularly in the identification of suspected neutral reaction products.

We have for some time been investigating the electron-bombardment, matrix-isolation spectroscopy (EBMIS) technique as a complementary tool to modern mass spectrometric techniques for studies of gas-phase ion processes. This approach has allowed us to characterize several gas-phase ion systems and their products, including the neutral enol isomer of acetone, 1-propene-2-ol,[1] and to observe the known isodihalomethanes as products of ionization of dihalomethanes.[2] We have found the EBMIS technique to be a useful means by which to generate thermodynamically unstable isomers of neutral precursors. These are believed to be formed through matrix isolation of the neutral and ionic products of gas-phase ion processes, followed by neutralization of matrix-isolated ions by secondary electrons to generate the neutral counterpart of stable cationic species.

Recently, we have begun to investigate this technique as an approach to the formation and characterization of ionic organometallic species in the matrix-isolation environment. This paper reports on our first system of study, involving electron bombardment of iron pentacarbonyl, $Fe(CO)_5$. The choice of this molecule has proven to be fortuitous, because it yields readily both cationic and anionic subcarbonyl fragments from decomposition of energized $Fe(CO)_5^+$ and $Fe(CO)_5^-$, respectively.[3,4] Both species are expected to be generated as gas-phase transients under our experimental conditions in good yield. Thus, working with $Fe(CO)_5$ presents the opportunity to evaluate the relative efficiency with which such charged species are matrix isolated under our EBMIS conditions, with a precursor that is capable of generating both types of products. This is of particular interest, because a recurrent theme in our work has been the relative inefficiency with which cationic molecular ions and fragments are trapped. For example, the cationic molecular ion of acetone was never observed in our earlier work with acetone[1] despite its implied role in the production of 1-propen-2-ol.

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A great deal of research effort has been spent on characterizing the structure,[5−7] spectroscopy,[8,9] metal−ligand bond thermochemistry,[7,10−12] and photochemistry[13−18] of $Fe(CO)_5$. As well, there is considerable data on its neutral subcarbonyls $Fe(CO)_n$ (n=1−4), from matrix isolation,[13−15,19−23] and gas-phase studies[15,17,18] of the photochemistry of $Fe(CO)_5$, as well as from reactions of CO with thermally evaporated Fe atoms.[24] Anionic and cationic products from reactions of CO with atoms and atomic ions formed by laser ablation of Fe targets have also been recently reported by Zhou et al.[25] Higher nuclearity carbonyls of iron are also fairly well-known and characterized.[6,24,26]

Poliakoff and Turner[13,14,16] and Poliakoff[22] have extensively characterized the photochemical products of matrix-isolated $Fe(CO)_5$ following irradiation with UV light and have in particular studied the chemistry and structural properties of $Fe(CO)_4$ and $Fe(CO)_3$. Photodissociation of $Fe(CO)_5$ in highly dilute matrix samples is known to occur with UV light from a Hg arc lamp to form $Fe(CO)_4$, a process which may be efficiently reversed with irradiation of the product matrixes with light from a Nernst glower.[14] In the case of Xe and Kr matrixes, this process generates the rare gas complex $Fe(CO)_4RG$ (RG = Xe and Kr).[13] Production of lower subcarbonyl photolysis products, and even Fe atom production, was also reported upon prolonged UV irradiation. Breeze et al.[23] have generated spectra of the isotopically substituted anionic species $Fe(CO)_4^-$ in a rare gas matrix by electron bombardment of matrixes containing $Fe(CO)_5$, as well as various neutral subcarbonyls.

Several studies have been carried out on the gas-phase ion chemistry associated with $Fe(CO)_5$.[3,4,12,27−29] Ionization by charge exchange with Ar^+ and Xe^+ results in production of mostly Fe^+ and $FeCO^+$ (Ar) or $Fe(CO)_2^+$and $Fe(CO)_3^+$ (Xe) under low-pressure conditions.[28] Studies of electron-impact ionization of $Fe(CO)_5$ show the production of all possible cationic subcarbonyl products to be facile,[3,29] with Fe^+ and $Fe(CO)^+$ being the major cationic products. Dissociative electron attachment studies have demonstrated that electrons with very low energies can generate all subcarbonyl anions and the anionic atomic ion from $Fe(CO)_5$, with electrons in the 0−12 eV energy range.[4] As well, there are numerous experimental and theoretical studies on the thermochemistry of the sequential ligand loss from the anionic[12,30] and cationic[3,29,31−33] molecular ions.

$Fe(CO)_5$ is therefore an ideal test molecule for studies of the charged and neutral products of ionization generated by various mechanisms such as direct electron impact, charge transfer, Penning ionization, and secondary electron dissociative attachment in the EBMIS environment. All possible charged products are energetically accessible and have been observed previously with electrons of energy less than or equal to that of those employed in this work. The observation of certain products and not others in the present work is a valuable tool for understanding the particular processes that give rise to the major products, a major uncertainty in previous EBMIS work.

Experimental Details

The EBMIS technique has been described in previous publications.[34] Briefly, Ar (prepurified 99.998%, Matheson), Kr (research grade, 99.998%, Matheson), Xe (research grade, 99.995%, Matheson), CH_4 (UHP grade, 99.97% Matheson), N_2 (prepurified, 99.998% Matheson), Ar containing 4% CH_4, or Ar containing 2% N_2 were combined with freeze−pump−thaw degassed $Fe(CO)_5$ (>99% chemical purity, Aldrich) to generate a 1:1000 (Fe:matrix gas) mole ratio mixture (unless otherwise noted). Gas mixtures were passed through a 150−300 eV beam of electrons and then condensed on a 16 K CsI spectroscopic window. Electrons were generated thermionically from a resistively heated thoriated tungsten filament, accelerated parallel to the surface of the matrix substrate, toward a brass anode plate located just beyond the matrix substrate holder. Depositions at a flow rate of 1.0 standard cubic centimeter per minute were typically done over a 4 h period. Products were characterized by FTIR spectroscopy with a 0.8 cm^{-1} resolution Bomem MB-102 spectrometer, equipped with a dry-air purge. Matrices were further characterized by thermal annealing using a Scientific Instruments Inc. 9600-1 Silicon Diode Temperature Controller, as well as by irradiation with filtered light from a high-pressure Xe arc lamp (Kratos LH150).

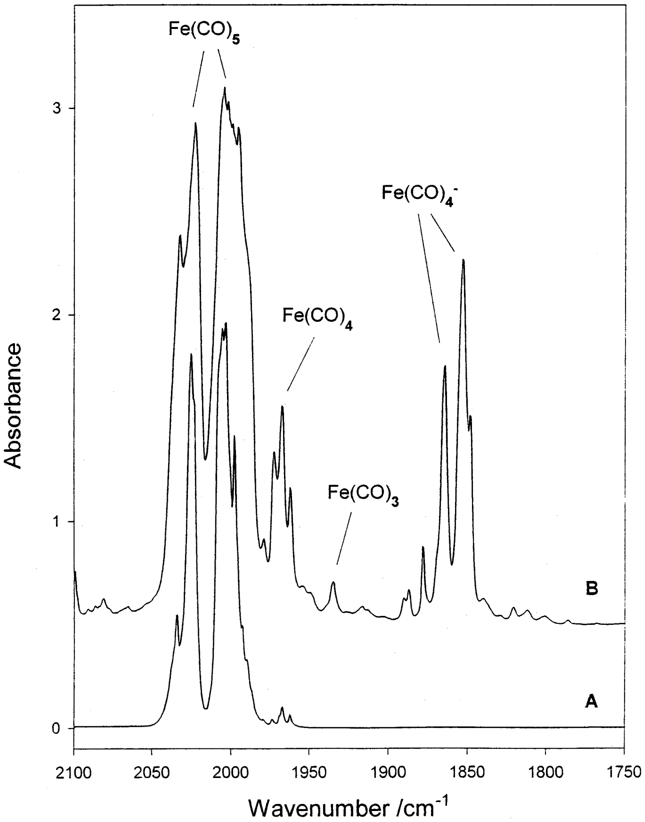

Figure 1. Infrared spectra in the carbonyl stretching mode region of matrixes formed by 4-h deposition of Ar gas containing 0.1% $Fe(CO)_5$ (A) without electron bombardment and (B) with electron bombardment.

Results

Gas-phase electron bombardment and subsequent matrix isolation of samples of Ar containing 1:1000 $Fe(CO)_5$:Ar resulted in spectroscopic signals associated with several previously identified subcarbonyls of iron, as shown in Figure 1 and summarized in Table 1. The identified products are the neutral molecules $Fe(CO)_4$,[13,19] $Fe(CO)_3$,[22] and $Fe(CO)_2$,[25] as well as the anionic products $Fe(CO)_4^-$ [23,25] and $Fe(CO)_3^-$. The major products are the neutral and anionic tetracarbonyls with roughly equivalent yields in terms of signal intensity. Yields of lower subcarbonyls were much lower for both the neutrals and anions. Analogous samples prepared from Kr and Xe containing 1:1000 $Fe(CO)_5$ revealed similar products, several of which are identified here for the first time in Kr and Xe matrixes. Yields of $Fe(CO)_4^-$ in Kr and Xe are lower with respect to Ar, based upon signal intensity. In addition, $Fe(CO)_4Xe$[13] is clearly identified in Xe (see below). Inclusion of small amounts of CH_4 or N_2 in Ar gas mixtures resulted in qualitatively similar spectra

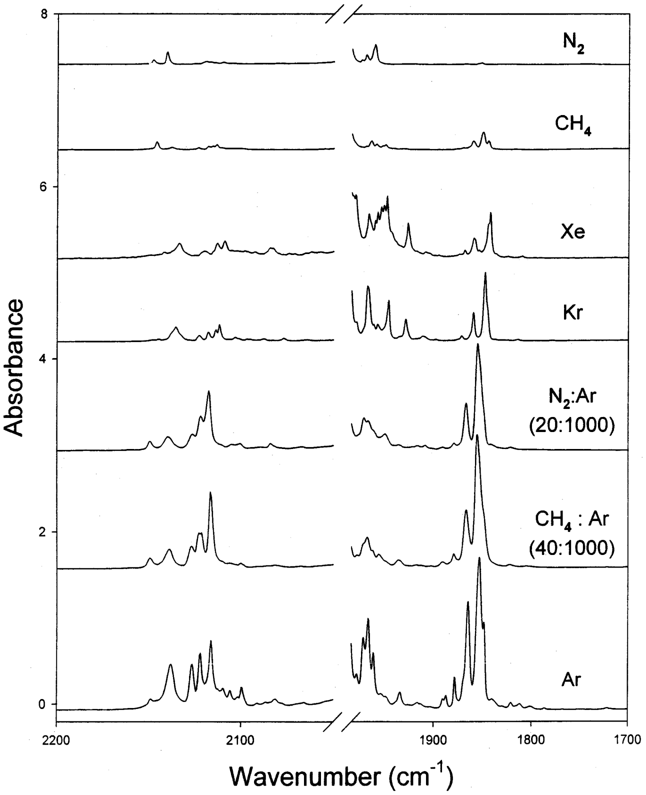

Figure 2. Portions of infrared spectra of matrixes formed by electron bombardment of 1:1000 $Fe(CO)_5$ in various gas mixtures. In ascending order: pure Ar, 4% CH_4 in Ar, 2% N_2 in Ar, pure Kr, pure Xe, pure CH_4, pure N_2.

TABLE 1: Major Infrared Absorption Wavenumbers for Observed Neutral and Anionic Fragments of $Fe(CO)_5$ Decomposition Following Electron Bombardment of $Fe(CO)_5$ in Ar, Kr, and Xe

argon /cm^{-1}	ref	krypton /cm^{-1}	ref	xenon /cm^{-1}	ref	assignment
1995.5	13	1994.0	*a*	1988.8	13	$Fe(CO)_4$
1988.3	13	1986.9	*a*	1979.9	13	$Fe(CO)_4$
1972.7	13	1968.4	*a*	1966.5	13	$Fe(CO)_4$
1934.9	22	1929.5	22	1926.7	22	$Fe(CO)_3$
1878.2	25	1871.0	*a*	1867.6	*a*	$Fe(CO)_2$
1864.7	23	1859.7	*a*	1858.4	*a*	$Fe(CO)_4^-$
1853.2	23, 25	1847.7	*a*	1841.7	*a*	$Fe(CO)_4^-$
1786.3	25	1778.1				$Fe(CO)_3^-$

[a] This work

following electron bombardment, but with relatively diminished $Fe(CO)_4$ compared with $Fe(CO)_4^-$ (see Figure 2) and a reduced yield of all products. In contrast, EB of $Fe(CO)_5$ in pure CH_4 resulted in greatly diminished yields of all products (<10%), and EB of $Fe(CO)_5$ in pure N_2 gave no observable products at all (Figure 2).

Annealing of samples formed by EB of Ar containing $Fe(CO)_5$ at as low as 20 K clearly showed loss of features associated with $Fe(CO)_4$ and $Fe(CO)_4^-$. The extent of this transformation increased with annealing temperature; however, the total change was modest even after 5 min of annealing at 36 K. The major product(s) show carbonyl absorptions at 2063.5 and 2040.9 cm^{-1} due to $Fe_2(CO)_9$[26] and a band at 1985 cm^{-1} due to another unidentified higher-order carbonyl species (see Figure 3).

Irradiation of samples formed by EB of Ar containing 1:1500 $Fe(CO)_5$ with visible light (>400 nm) resulted in partial depletion of $Fe(CO)_4$ and $Fe(CO)_3$, with concomitant growth of $Fe(CO)_5$ (see Figure 4). Subsequent irradiation with the complete output of the Xe arc lamp resulted in partial depletion of $Fe(CO)_5$ and complete loss of those due to $Fe(CO)_4^-$, with significant production of $Fe(CO)_4$ as the major product and some $Fe(CO)_3$ (Figure 5). Depletion of $Fe(CO)_4^-$ was correlated with loss of a set of bands at 2166.1, 2119.0, 2122.4, and 2126.7 cm^{-1}, tentatively assigned to CO trapped in close proximity to $Fe(CO)_4$, as discussed below. The concomitant loss of these bands was observed in all matrix mixtures tested in which $Fe(CO)_4^-$ was generated.

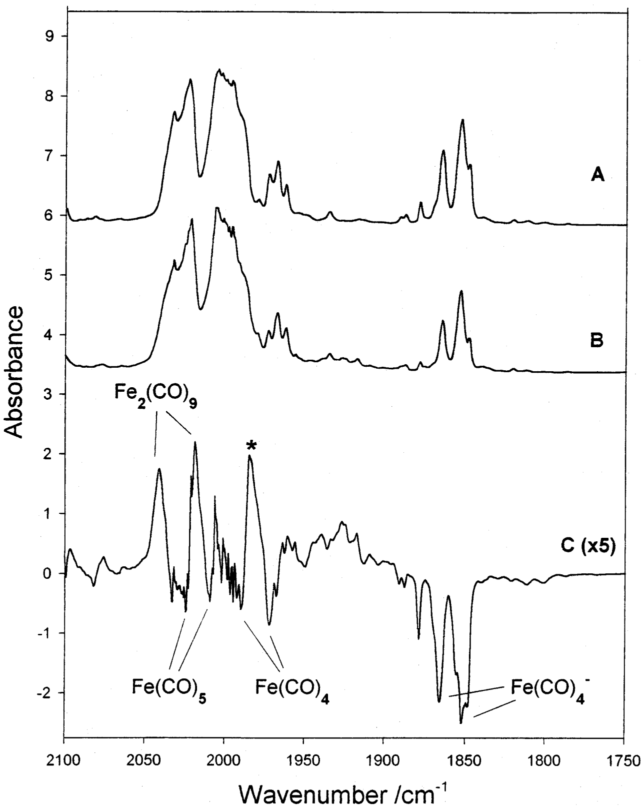

Figure 3. Infrared spectra in the carbonyl stretching mode region of matrixes formed from Ar gas containing 0.1% $Fe(CO)_5$ (A) on deposition at 16 K, (B) following annealing to various temperatures up to 36 K for a total of 2.5 h, followed by cooling to 16 K, and (C) difference spectrum (B-A), magnified 5×. Asterisk denotes unidentified higher-nuclearity iron carbonyl species.

Visible irradiation of a sample formed by EB of $Fe(CO)_5$ in Xe showed loss of $Fe(CO)_5$, $Fe(CO)_4$, and significant loss of well-defined features at 1953.7, 1950.8, and 1947.9 cm^{-1} and a weak band at 2082.9 cm^{-1} which are very similar to those that have been assigned to $Fe(CO)_4Xe$.[13] Irradiation with the full lamp output caused these features to partially reappear, with further loss of $Fe(CO)_5$, $Fe(CO)_4$, and $Fe(CO)_4^-$. No other major products were observed in the Xe experiment, although a broad feature could be seen underlying the entire carbonyl stretching region of $Fe(CO)_5$ and $Fe(CO)_4$. Similar photochemistry was observed in Kr matrixes, except that loss of $Fe(CO)_4^-$ was not complete. We observe a triplet of peaks that behaves much as $Fe(CO)_4Xe$, at 1958.4, 1956.5, and 1952.2 cm^{-1}, which Poliakoff and Turner have noted may be due to the analogous $Fe(CO)_4Kr$ complex.[13] We feel this assignment is correct given the close similarity in the behavior of the two sets of features in Xe and Kr matrixes, which is that they are easily photobleached with visible light, but are regenerated with UV−visible irradiation. These features were obscured on deposition, but easily distinguishable in difference spectra following irradiation.

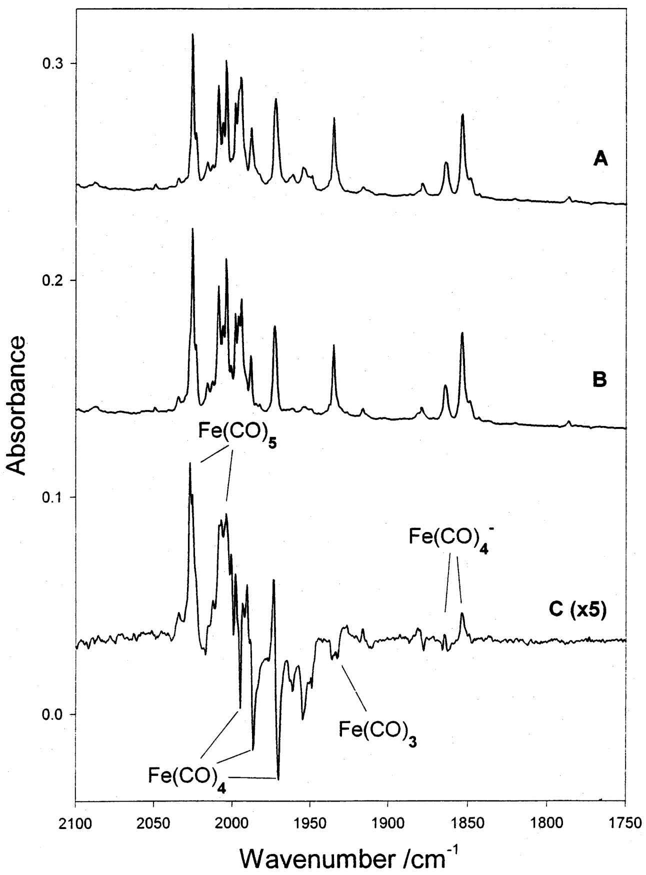

Figure 4. Infrared spectra in the carbonyl stretching mode region of matrixes formed from Ar gas containing 0.15% Fe(CO)$_5$ (A) on deposition (B) following 15 min irradiation with >400 nm light and (C) difference spectrum (B−A) magnified 5× vertically.

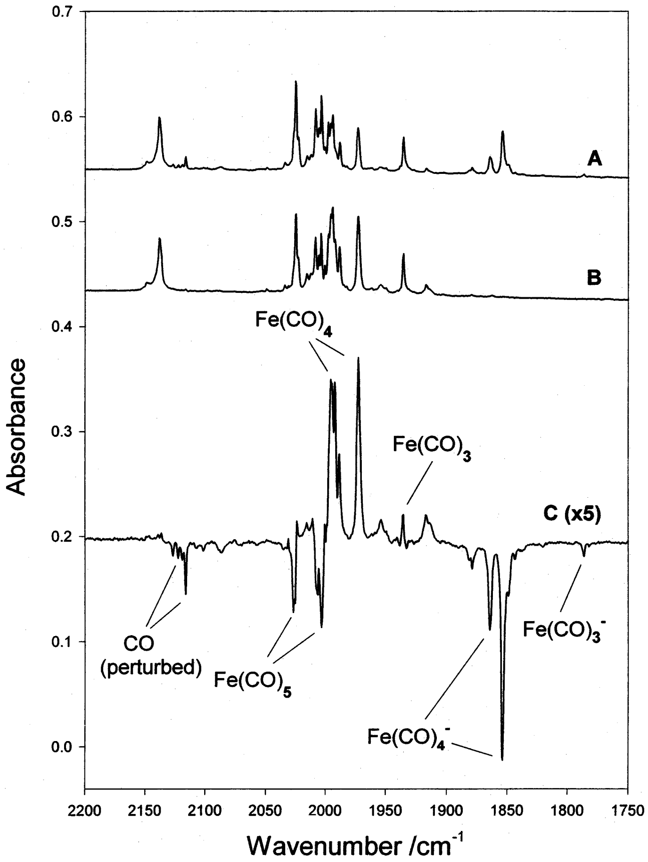

Figure 5. Infrared spectra in the carbonyl stretching mode region of matrixes formed from Ar gas containing 0.15% Fe(CO)$_5$ (A) on deposition following 15 min irradiation with >400 nm light, (B) following subsequent 15 min irradiation with <400 nm light, and (C) difference spectrum (B−A) magnified 5× vertically.

Discussion

The results presented above demonstrate that gas-phase electron bombardment of several rare gases and gas mixtures containing small amounts of Fe(CO)$_5$, followed by matrix isolation of the gaseous product mixture thus generated, results in the isolation in good yield of the tetracarbonyl neutral and anionic carbonyl fragments, with smaller amounts of the lower subcarbonyls. These results are qualitatively similar to those obtained by Breeze et al.[23] from 500 to 800 eV electron bombardment of previously prepared matrixes containing Fe(CO)$_5$. However, production and isolation of Fe(CO)$_4^-$ under EBMIS conditions is substantially more efficient than by electron bombardment or UV irradiation of previously prepared matrixes containing Fe(CO)$_5$, based upon published spectra.[14,23] The relatively high yield of Fe(CO)$_4$ and Fe(CO)$_4^-$ obtained by EBMIS reflects the advantage of carrying out the high-energy electron bombardment step in the gas phase above and parallel to the matrix surface during sample preparation. Processes such as carbonyl dissociation are free from significant cage effects when they occur in the gas phase before condensation of the mixture on the cold substrate. EBMIS yields are expected to reflect products of rapidly occurring gas-phase dissociation processes; subsequent trapping and stabilization of these products is expected to efficiently quench any further reactions such as decomposition of metastable, vibrationally excited products.

Gas-phase electron impact (EI) work demonstrates that production of cationic subcarbonyls and even the cationic atomic ion (Fe$^+$) are rapid and efficient processes.[3,28,29] Under typical gas-phase conditions used with EI ionization in mass spectrometry (50−70 eV electrons, high vacuum), Fe$^+$ and FeCO$^+$ are the major products, although Fe(CO)$_5^+$ and all other subcarbonyl cations are also produced as significant minor products.[29] At much lower electron energies, such as 12−20 eV, production of higher subcarbonyls and even Fe(CO)$_5^+$ is dominant.[35] Charge-transfer ionization with Ar$^+$ and Xe$^+$ at very low pressures yields primarily highly decarbonylated products such as Fe$^+$ and FeCO$^+$ with Ar$^+$ and Fe(CO)$_2^+$ and Fe(CO)$_3^+$ with Xe$^+$.[28] If it is assumed that the observed neutral fragments in our work are due to neutralization of cationic products of Fe(CO)$_5^+$ decomposition, the absence of significant yields of any neutral subcarbonyls below Fe(CO)$_3$, and the fact that Fe(CO)$_4$ is the major neutral product in our work, indicates that the EBMIS conditions are significantly altering the gas-phase ion chemistry of Fe(CO)$_5^+$. It would then be reasonable to conclude that primary decomposition products that would otherwise go on to further decomposition are efficiently stabilized in the EBMIS environment.

It is noteworthy that the electron impact conditions of typical mass spectrometric studies are significantly different from our EBMIS conditions, in which the target molecule is immersed in an excess of another gas. In this context, it is statistically much more likely that the matrix support material gas will be ionized and not Fe(CO)$_5$. In light of this, the results of our EBMIS studies are expected to be more relevant to gas-phase ion chemistry studies employing higher pressure chemical ionization sources. Thus, the major ionization process for formation of cationic Fe(CO)$_5^+$ is expected to be charge-transfer ionization and not direct EI. However, as noted above, studies of charge-transfer ionization of Fe(CO)$_5$ and its subsequent decomposition show even more dramatic decomposition of $Fe(CO)_5^+$, with no significant production of any subcarbonyl cationic species above $FeCO^+$. Therefore, observation of only modest ligand loss processes in our work remains a significant difference with respect to gas-phase conditions, when compared with either typical direct EI or indirect charge-transfer ionization at low pressures. This difference infers strongly that efficient quenching of the excess energy initially present in the $Fe(CO)_5^+$ cation occurs during the process of gas condensation and matrix isolation that follows the ionization step.

The relative decrease in $Fe(CO)_4$ yield upon addition of small amounts of N_2 or CH_4 with respect to experiments in pure rare gases is consistent with these ideas, because vibrational energy transfer to polyatomic molecules is expected to be much more efficient compared with rare gas atoms. Thus, the decrease in $Fe(CO)_4$ yield may reflect enhanced energy transfer from the initially formed $Fe(CO)_5^+$ to N_2 or CH_4 and a corresponding decrease in extent of fragmentation. This effect is even more pronounced in pure CH_4 and N_2, where little or no fragmentation is observed (see Figure 2). Analogous evidence for highly efficient stabilization of primary ionization products has also been seen in our previous work on oxalyl chloride.[34]

The absence of *any* cationic products in our work has different and more fundamental implications. Simple reasoning would predict that we would observe at least $Fe(CO)_5^+$ as a primary product of charge-transfer ionization or its primary cationic decomposition product $Fe(CO)_4^+$. The absence of cationic fragment products suggests strongly that efficient neutralization of such cationic species in the matrix is occurring, to yield the corresponding matrix-isolated neutral species. In the present case, cationic species present in the matrix are thought to be neutralized by capture of low-energy secondary electrons. The energy released in this step is efficiently transferred to the matrix, as has been demonstrated in the past by the fact that relatively unstable isomers such as neutral 1-propen-2-ol may be isolated following EBMIS.[1] Thus, the absence of the expected primary products of $Fe(CO)_5^+$ decomposition in the gas phase, $Fe(CO)_4^+$ and $Fe(CO)_3^+$, remains consistent with primary production of these species in our experiment, provided these products are rapidly stabilized, matrix isolated, and then efficiently converted to $Fe(CO)_4$ and $Fe(CO)_3$. Note that if such a process were to occur in the *g*as-phase, it would be expected to lead to significant secondary fragmentation of $Fe(CO)_4$ and $Fe(CO)_3$, generating lower subcarbonyls and Fe atoms, as the energy released would be of the order of 8 eV[12] .

It is well-known that isolation and detection of cationic species in rare gas matrixes formed from gases other than Ne (i.e., Ar, Kr, or Xe) is difficult.[2,36] This effect is believed to be due to cation neutralization following efficient spontaneous electron transfer from isolated electron traps in the matrix, such that the cations of species with ionization potentials (IPs) within 6 eV of the IP of Ar (for example) cannot generally be isolated in an Ar matrix. In the present work, the cations that we would expect to observe following EI of $Fe(CO)_5$ are all known to have neutral counterpart IPs in the range of 6.66−8.03 eV,[12] such that their observation should be possible by this rule. We therefore consider capture of scattered secondary electrons to be a more viable explanation for the absence of cationic products in this work.

Production of anionic species under our conditions is most likely due to direct gas-phase, dissociative capture of scattered and secondary low-energy electrons by $Fe(CO)_5$. A significant increase in current registered at the Faraday plate under active electron bombardment conditions, compared to when no gas is flowing, indicates a multiplication of electrons by a factor of at least four, such that a plentiful supply of secondary electrons of various energies is expected to be present in the sample preparation area. Compton and Stockdale[4] have shown that low-energy electrons in the 0−10 eV energy range can generate all anionic subcarbonyls as well as Fe^- under slow-electron collision conditions in the gas phase. If no gas-phase collisional stabilization were occurring, the product yield observed in our work would correspond to production of fragments from electrons in the 0−2 eV range. In this range, production of $Fe(CO)_4^-$ is the major process, with $Fe(CO)_3^-$ production significantly less and production of lower subcarbonyls essentially nonexistent. However, given the modest extent of carbonyl loss in the neutral spectra discussed above, it is likely that some quenching of sequential carbonyl loss is occurring in our work, because of the relatively high pressure in the sample generation region of the apparatus, estimated at 0.1−0.5 Torr.

Note that the mechanism proposed above for neutralization of cationic fragment products could be extended to account for the formation of matrix-isolated anionic species via electron capture by the matrix-isolated neutral subcarbonyls of $Fe(CO)_5$. In this connection, it is noteworthy that all neutral subcarbonyls of $Fe(CO)_5$ have significantly positive electron affinities.[37] However, although we cannot rule out this process, the efficient formation of all anionic subcarbonyls of $Fe(CO)_5$ following dissociative electron capture is a simpler and more direct explanation for the observation of anionic fragment products. As well, the presence of small amounts of CH_4 and N_2 in Ar appears to favor production of $Fe(CO)_4^-$ over $Fe(CO)_4$, which could not be easily explained if $Fe(CO)_4^-$ were generated from $Fe(CO)_4$. If the anion were generated from its neutral counterpart, one would expect the yield of $Fe(CO)_4^-$ to track that of $Fe(CO)_4$. As it does not, our results are most consistent with a mechanism in which two independent processes give rise to these two major products.

Photochemical studies carried out in the present work do not reveal significant new insights, as the observed behavior is analogous to previous matrix-isolation studies of the photochemistry of $Fe(CO)_5$.[13,14,16,22] Thus, we observe the expected recombination of matrix-isolated $Fe(CO)_4$ and CO under visible irradiation and destruction of $Fe(CO)_5$ under UV−visible irradiation. We also observe the correlated destruction of $Fe(CO)_4^-$ and features at 2166.1, 2119.0, 2122.4, and 2126.7 cm^{-1}. Such depletion has been previously observed in electron bombardment studies of preformed Ar matrixes containing $Fe(CO)_5$ by Breeze et al.,[23] who attributed these bands to matrix-isolated CO^+. However, Thompson and Jacox have definitively measured the fundamental position of CO^+ isolated in a Ne matrix at 2194.4 cm^{-1}.[38] Therefore, we feel it is more likely that these features are associated with CO trapped in close proximity to $Fe(CO)_4^-$. The shift in these bands with respect to the wavenumber position of unperturbed CO in Ar (2136 cm^{-1}) is attributed to a weak perturbation of CO, which is lifted when $Fe(CO)_4^-$ is destroyed by photoinduced electron transfer to an unidentified counterion in the matrix.

Conclusions

Our work demonstrates that the study of gas-phase ion decomposition processes with the EBMIS technique is partially successful, in that efficient isolation and characterization of anionic products is observed. The absence of cationic iron carbonyl products demonstrates the fundamental drawback of the technique, which is that the neutral counterparts of cations of interest are often preferentially isolated, most likely due to secondary electron capture in the matrix. The absence of significantly decarbonylated products indicates that efficient collisional stabilization of primary gas-phase ion decomposition products is occurring. Taken together, these conclusions indicate that the EBMIS approach is ideal for the formation, isolation and characterization of anionic primary products resulting from low-energy electron capture processes and for formation of neutral species generated via neutralization of cationic molecular ion decomposition products.

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