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Reactions of Sc^+, Ti^+, V^+, Fe^+, Co^+, and Ni^+ with Naphthalene Halides. Study of the Initial Steps of a Metal-Catalyzed Polymerization in the Gas Phase

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Poly(naphthylene) is of interest, in particular, due to its intrinsic electrical conductivity. Reported here are the initial steps in the metal-catalyzed polymerization of naphthalene as observed in the gas-phase reactions of Sc^+, Ti^+, V^+, Fe^+, Co^+, and Ni^+ with 1-halonaphthalenes studied in a Fourier transform mass spectrometer. Sc^+, Ti^+, V^+, and Fe^+ were found to dehydrohalogenate all of the halides stepwise, to produce ions of the form $M(C_{10}H_6)_n{}^+$. Up to 6 steps of dehydrohalogenations were observed in the case of the reactions of Fe^+ with 1-chloronaphthalene. Co^+ and Ni^+ exhibited similar behavior except in the case of 1-fluoronaphthalene, where only condensation products were observed. Sc^+ showed unusual reactivity by also being able to eliminate C_2H_2, this reaction being most prominent in the case of fluoronaphthalene. Aside from dehydrohalogenations, Ti^+ was found to eliminate a hydrogen atom to form $TiC_{10}H_6X^+$ in its reactions with all of the halides. 2-Bromonaphthalene was also studied and compared with the results for 1-bromonaphthalene, but no significant differences were observed. Secondary and higher order reactions were investigated, and several ionic products from primary and secondary reactions were studied by collision-induced dissociation (CID). The formation of $(C_{10}H_6)_n{}^+$ with $n = 2$ and 3 was observed and was in some cases formed by loss of M or MX from $M(C_{10}H_6)_n{}^+$ and $M(C_{10}H_6)_nX^+$, respectively, but also in direct reactions of $M(C_{10}H_6)_{n-1}{}^+$ with the neutral halonaphthalene, which is in contrast with the behavior observed for the related phenyl halides in an earlier study. The ionization potentials of $(C_{10}H_6)_n$ with $n = 2$ and 3 are lower than that of iron (7.87 eV) as Fe was lost upon CID of $Fe(C_{10}H_6)_n{}^+$ for $n = 2$ and 3. The thermodynamical consequences of the reactions are discussed, as well as deductions concerning the structure of several of the ionic reaction products.

Introduction

Reactions of metal ions with organic molecules in the gas phase have been extensively studied in recent years by several research groups as evidenced in a recent review paper.[1] Aside from curiosity pertaining to the reaction paths, these studies can give information regarding the thermodynamics and kinetics of the reactions and provide a valuable insight into the role of metals as catalysts.

More than a decade ago Dietz, Chatellier, and Ridge[2] reported on the reactions of Fe^+ with the phenyl halides in the gas phase as studied by ion cyclotron resonance spectroscopy. Instrumental advances, in particular the development of Fourier transform mass spectrometers, have opened doors to more detailed analysis of ion−molecule reactions in the gas phase. In a recent paper, the reactions of Fe^+ with phenyl halides in the gas phase were reported[3] and later the reactions of all the other first-row transition metal ions were studied.[4] In addition, Huang and Freiser have reported on the reactions of Fe^+ with chlorobenzene using similar techniques,[5] and Freiser's group has also studied the reactions of $M(benzyne)^+$ with various substrates.[5,6] Among the interesting reactions observed in the studies mentioned above was the iron-catalyzed formation of oligomers of phenylene of the form $(C_6H_4)_n{}^+$, with $n = 2-5$, from iron complex ions of the form $Fe(C_6H_4)_n{}^+$, which in turn were produced in successive dehydrohalogenation reactions of Fe^+ with the phenyl halides. This catalytic behavior was also observed for some of the other first-row transition metal ions, but each ion behaved uniquely.

We have been examining other systems to further probe the phenomenon of metal-catalyzed polymerization in the gas phase as part of our effort to characterize the gas-phase reactions of transition metal ions with aromatic compounds[7] and reported here are the reactions of several transition-metal ions with the 1-halonaphthalenes. The reactions of these metal ions with 1-fluoronaphthalene have been discussed in a preliminary report.[8] The metal ions were chosen in light of the results obtained in the phenyl halide study,[4] where Cr^+, Mn^+, Cu^+, and Zn^+ were found to be either unreactive or only participate in reactions of little

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interest, such as the charge exchange reactions of Zn^+ (due to its high ionization potential).

Poly(naphthylene)[9] (PN) is of particular interest due to its intrinsic electrical conductivity,[10,11] whereas most other conductive polymers require doping to achieve the conductive state. PN has been prepared by a number of different synthetic routes including recently developed Friedel-Craft reactions,[12] electrochemical polymerization,[13] and plasma polymerization.[14] Further, the metal-catalyzed polymerization of naphthalene and chloronaphthalene by the Kovacic method has been reported by Hsing et al.,[15] and also reported is the nickel-catalyzed polymerization of dibromonaphthalenes to produce relatively large polynaphthylenes.[16] Aside from uses as a conductive polymer, PN has found other uses, such as serving as a support for catalytically active materials.[17]

In the case of the phenyl halides, the unmetalated oligomer species, $(C_6H_4)_n^+$, was formed from $M(C_6H_4)_n^+$, and similar behavior was expected in the case of the naphthalene halides. Unexpected differences were, however, observed in some cases, and more reactivity, in the sense of a wider variety of primary reaction products, was observed in the reactions of the metal ions with the naphthalene halides than with the phenyl halides, particularly for Sc^+ and Ti^+.

Experimental Section

The experimental approach has been described elsewhere,[3,4,7] but briefly, the experiments were done by employing a Millipore-Extrel FTMS-2000 Fourier transform mass spectrometer equipped with a pulsed CO_2 laser and a laser desorption interface. The experiments involving Fe^+ and Ti^+ were initially performed using a Nicolet FTMS-2000 instrument equipped with cryo- and turbomolecular pumps instead of the standard diffusion pumps. A very "clean" and low background pressure ($<1 \times 10^{-9}$ Torr) was achieved with this arrangement. Some of the high-mass species reported here were difficult or impossible to detect when the experiments were repeated using a "standard" diffusion-pumped instrument. See the Pressure Dependence section for a further discussion regarding this issue.

The metal ions were generated by using the laser desorption method developed by Freiser and co-workers,[18] and isolated using double resonance techniques[19] prior to monitoring the reactions with each naphthalene halide, which was present in the cell of the mass spectrometer at a static pressure. Sc^+, Ti^+, and V^+ were produced by laser desorption of the pure metals, and Fe^+ and Ni^+ from stainless steel, but Co^+ was produced by laser desorption from the chloride salt instead of the pure metal, as the metal is ferromagnetic. The method of using laser ionization of salts instead of pure metals has been discussed by Weil and Wilkins.[20]

All reaction paths were confirmed by using double-resonance techniques. Argon or nitrogen buffer gas, maintained at 40−100 times the pressure of the sample gas, was used in a duplicate set of experiments to minimize the abundance of "hot" metal ions. It should be noted, however, that by operation at only slightly above the threshold laser fluence for metal ion production, the production of ions in excited states is low, much lower than that produced by electron impact. This was realized by performing a study of the reactions of $Fe(CO)_5$ with Fe^+ produced by electron impact and laser desorption (varying the power density) and comparing the results with those from the study of the reactions of $Fe(CO)_5$ with Fe^+ in excited states, which has been reported by Russell's group.[22] It should also be noted that the use of buffer gases may increase the abundance of adducts, formed in association reactions, which benefit from the higher pressure. No significant differences were observed in the reactivity of the metal ions with or without the buffer gas present, aside from the increased formation of adducts, which precluded the observation of many of the higher mass ions produced in higher order reactions (see also below in Pressure Dependence section).

Mass spectra were acquired in the broadband mode with bandwidths of 1000 or 1200 KHz, using 32K or 64K data points, and obtained after reaction times ranging from 0.003 to 128 s. The sample was incorporated through the batch inlet system, and the pressure of the neutral in the FTMS cell was varied from 1×10^{-8} to 2×10^{-7} Torr. Some of the higher order reactions were found to be pressure dependent, as discussed below. The naphthalene halides were commercially obtained and used without further purification, except for a few freeze−pump−thaw cycles to remove dissolved gases. 1-Halonaphthalenes were used throughout, except that 2-bromonaphthalene was used to study if different reactivity was experienced for the two different isomers.

Results and Discussion

The products from the *primary* reactions of the metal ions with the naphthalene halides are listed in Table 1. Below is a discussion of some of these reactions, where we feel that the results are unusual or of special interest, and an account of the secondary and higher order reactions that were observed and could be characterized.

Primary Reactions. The most common reaction observed in the study, as was the case with the related phenyl halide study, is dehydrohalogenation, as shown in reaction 1. All of the metal ions participated in reaction 1 with all of the halides, except that neither Co^+ nor Ni^+ did so in the case of fluoronaphthalene.

$$M^+ + C_{10}H_7X \rightarrow M(C_{10}H_6)^+ + HX \qquad (1)$$

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[9] The nomenclature adopted here is from the benzene analogues. C_6H_4 is referred to as benzyne, and $C_{10}H_6$, as naphthalyne; corresponding are terms such as poly(*p*-phenylene) and poly(1,4-naphthylene). Other conventions can be found in the literature, such as poly(1,4-naphthalene). Still others prefer dehydronaphthalene for $C_{10}H_6$. The most accurate terms, although somewhat lengthy, are 1,2-didehydrobenzene for *ortho*-benzyne, or simply benzyne, and the analogous and self-explanatory 2,3-didehydronaphthalene.

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Table 1. Primary Reactions of M^+ with Naphthalene Halides

	naphthalene halide reacns			
M	F	%	Cl	%
Sc^+	$ScC_{10}H_6^+ + HF$	70	$ScC_{10}H_6^+ + HCl$	97
	$ScC_8H_5F^+ + C_2H_2$	30	$ScC_8H_5Cl^+ + C_2H_2$	3
Ti^+	$TiC_{10}H_6^+ + HF$	65	$TiC_{10}H_6^+ + HCl$	93
	$TiC_{10}H_6F^+ + H$	35	$TiC_{10}H_6Cl^+ + H$	7
V^+	$VC_{10}H_6^+ + HF$	100	$VC_{10}H_6^+ + HCl$	100
Fe^+	$FeC_{10}H_6^+ + HF$	100	$FeC_{10}H_6^+ + HCl$	50
			$C_{10}H_7^+ + [FeCl]$[a]	50
Co^+	$CoC_{10}H_7F^+$	100	$CoC_{10}H_6^+ + HCl$	100
Ni^+	$NiC_{10}H_7F^+$	100	$NiC_{10}H_6^+ + HCl$	80
			$C_{10}H_7^+ + [NiCl]$[a]	20

	naphthalene halide reacns			
M	Br	%	I	%
Sc^+	$ScC_{10}H_6^+ + HBr$	97	$ScC_{10}H_6^+ + HI$	80
	$ScC_8H_5Br^+ + C_2H_2$	3	$C_{10}H_7^+ + [ScI]$[a]	20[b]
Ti^+	$TiC_{10}H_6^+ + HBr$	60	$TiC_{10}H_6^+ + HI$	50
	$TiC_{10}H_6Br^+ + H$	40	$TiC_{10}H_6I^+ + H$	20
			$C_{10}H_7^+ + [TiI]$[a]	30[b]
V^+	$VC_{10}H_6^+ + HBr$	65	$VC_{10}H_6^+ + HI$	50
	$VC_{10}H_6Br^+ + H$	35	$C_{10}H_7^+ + [VI]$[a]	50[b]
Fe^+	$FeC_{10}H_6^+ + HBr$	40	$FeC_{10}H_6^+ + HI$	10
	$C_{10}H_7^+ + [FeBr]$[a]	60	$C_{10}H_7^+ + [FeI]$[a]	10
			$FeC_{10}H_7^+ + I$	80
Co^+	$CoC_{10}H_6^+ + HBr$	100	$CoC_{10}H_6^+ + HI$	15
			$CoI^+ + C_{10}H_7$	15
			$CoC_{10}H_7^+ + I$	70
Ni^+	$NiC_{10}H_6^+ + HBr$	80	$NiC_{10}H_6^+ + HI$	40
	$C_{10}H_7^+ + [NiBr]$[a]	20	$C_{10}H_7^+ + [NiI]$[a]	20
			$NiC_{10}H_7^+ + I$	40

[a] Identity of neutral species unknown but assumed to be the metal halide. [b] The amount of $C_{10}H_7^+$ produced varied from one set of experiments to another. The numbers reflect the maximum relative amount observed. $M(C_{10}H_7X)^+$ is observed in the primary reactions in most cases. The relative abundance varies with pressure of the neutral, and as this abundance is of minor importance in this study, it is ignored in this table.

All of the metal ions were found to dehydroiodinate iodonaphthalene. In addition, Fe^+, Co^+, and Ni^+ were found to eliminate iodine to form $M(C_{10}H_7)^+$ and Co^+ was also found to react to form CoI^+. The ion MI^+ is isobaric with $M(C_{10}H_7)^+$, which can be problematic in the analysis of the product ions. Medium-resolution (ca. 5 K), internally calibrated measurements were of sufficiently high resolving power and mass accuracy to determine the identities and relative abundances for these ions, as listed in Table 1.

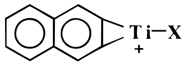
The production of $C_{10}H_7^+$ was observed in several cases in the primary reactions of the metal ions with the naphthalene halides, especially the iodide. $C_{10}H_7$ must have a lower IP than the metal halides in these reactions, as it retains the charge following the halogen abstraction by the metal. Unfortunately, the ionization potentials (IP) of most of the metal halides have not been critically evaluated, but the IP of FeI has been determined to be 7.8 ± 0.5 eV.[23] The relatively weak C−I bond is presumed to explain why the abstraction of iodine is favored over the other halogens.

Unique to Sc^+, and most prominent in the case of fluoronaphthalene, was the elimination of C_2H_2 to form $ScC_8H_5F^+$ according to reaction 2. This ion dehydrofluorinates fluoronaphthalene in a secondary reaction to form an ion at *m/z* 291 with the formula $ScC_{18}H_{11}F^+$. Collision-induced dissociation (CID) studies (60 eV) on $ScC_8H_5F^+$ gave inconclusive results in order to deduce a reasonable structure for this ion, and any speculations will not be put forth here.

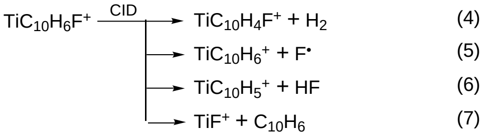
$$Sc^+ + C_{10}H_7F \rightarrow ScC_8H_5F^+ + C_2H_2 \qquad (2)$$

Ti^+ also exhibited a unique reaction to form $TiC_{10}H_6X^+$, which involves the elimination of a hydrogen atom as shown in reaction 3. This ion is relatively unreactive with the naphthalene halide except for a charge exchange reaction to form the halonaphthalene molecular ion. The formation of $TiC_{10}H_6X^+$ is unusual, but a possible structure is shown in **I**, consistent with CID studies (60 eV) of this ion when X = F that gave the results in eqs 4−7.

$$Ti^+ + C_{10}H_7X \rightarrow TiC_{10}H_6X^+ + H^\bullet \qquad (3)$$



I



Continuous ejection of $TiC_{10}H_6^+$ during the entire reaction time resulted in no reduction in the abundance of $TiC_{10}H_6X^+$ in the mass spectra, and further, continuous ejection of $TiC_{10}H_6X^+$ during the reaction time resulted in no reduction in the abundance of $TiC_{10}H_6^+$ in the mass spectra. This proves that neither ion is produced from the other and that both ions are products from primary reactions of Ti^+ with the naphthalene halides. It should be noted that the ejection time of an ion is several orders of magnitude shorter than the time between collisions at the pressures used in these experiments.

It is of interest to note that TiO^+ was shown not to react in this manner and formed only $TiO(C_{10}H_7Cl)^+$ at *m/z* 226 but no $TiO(C_{10}H_6Cl)^+$. The electrons tied up in the Ti−O bond appear to preclude the formation of a compound analogous to structure **I**.

Secondary and Higher Order Reactions. The primary reactions produced mainly $M(C_{10}H_6)^+$ in addition to $ScC_8H_5X^+$ and $TiC_{10}H_6X^+$. The reactions of the latter two ions have already been mentioned in the preceding section. Thus, we will limit our discussion here to the reactions of $M(C_{10}H_6)^+$ and the subsequent reactions of product ions from those secondary reactions.

The higher order reactions were considerably more varied for the naphthalene halides than the related phenyl halides.[3,4] Analogous to the phenyl halide case, a series of steps of dehydrohalogenation were observed in many cases, according to reaction 8 with $n = 1-5$.

$$M(C_{10}H_6)_n^{\ +} + C_{10}H_7X \rightarrow M(C_{10}H_6)_{n+1}^{\ +} + HX \qquad (8)$$

The largest complex ion observed was $Fe(C_{10}H_6)_6^+$ in

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Table 2. Maximum Number of Steps of Dehydrohalogenation

	naphthalene halide			
M	F	Cl	Br	I
Sc^+	2	2	2	1
Ti^+	2	3	3	1
V^+	3	3	2	1
Fe^+	2	6	4	1
Co^+	0	3	4	1
Ni^+	0	4	3	2

the case of the reactions of Fe^+ with chloronaphthalene. Table 2 lists how many steps of reaction 8 were observed for each metal ion with the naphthalene halides. Unmetalated oligomer ions of the form $(C_{10}H_6)_n{}^+$ were observed with $n = 2$ and 3, with the largest one most readily produced in the case of chloronaphthalene as the neutral reactant and Fe^+, Ti^+, and V^+ as the metal ions.

We will now limit the discussion to the Fe^+/chloronaphthalene system, which received the most detailed examination, and then discuss the other systems, highlighting similarities and differences in the behavior of the different metal ions and the different halides.

Competing with reaction 8 are two other reaction channels as shown in reactions 9 and 10. The formation

$$\mathrm{Fe(C_{10}H_6)_{\mathit{n}}^+ + C_{10}H_7Cl} \begin{cases} \longrightarrow \mathrm{(C_{10}H_6)_{\mathit{n}}^+ + [FeC_{10}H_7Cl]} & (9) \\ \longrightarrow \mathrm{(C_{10}H_6)_{\mathit{n}+1}^+ + [Fe + HCl]} & (10) \end{cases}$$

of $(C_{10}H_6)_n{}^+$ is observed for n up to 3. It should be noted that roughly 2/3 of the $(C_{10}H_6)_2{}^+$ was not produced through reaction 9, but directly in the reactions of $Fe(C_{10}H_6)^+$ with the neutral chloronaphthalene (reaction 10). This was established by continuously ejecting any ion at m/z 308 (the mass-to-charge ratio for $Fe(C_{10}H_6)_2{}^+$) during the entire reaction period, which resulted in a reduction of the $(C_{10}H_6)_2{}^+$ signal by a factor of 1/3. Double-resonance studies were used to prove that this ion could only be formed from $Fe(C_{10}H_6)^+$ and/or $Fe(C_{10}H_6)_2{}^+$. Similarily, continuous ejection of m/z 434 ($Fe(C_{10}H_6)_3{}^+$) resulted in a 40% reduction in the abundance of $(C_{10}H_6)_3{}^+$. Thus, 60% are produced directly in the reactions of $Fe(C_{10}H_6)_2{}^+$ with the neutral chloronaphthalene (reaction 10). This is in contrast with the behavior observed for the phenyl halides,[3,4] where for example *all* of the diphenylene ions were produced from $Fe(C_6H_4)_2{}^+$ and *all* of the triphenylene ions were produced from $Fe(C_6H_4)_3{}^+$. Figure 1a shows a mass spectrum obtained after a suitable reaction time and subsequent isolation of $Fe(C_{10}H_6)_3{}^+$ at m/z 434 using double-resonance techniques. The spectrum in Figure 1b was obtained after the isolated ion in spectrum 1a had been allowed to react for 5 s with the neutral chloronaphthalene maintained at a static pressure of 2×10^{-8} Torr. It is clear from the spectrum that the reaction gives two product ions: $Fe(C_{10}H_6)_4{}^+$ (at m/z 560) and $(C_{10}H_6)_3{}^+$ (at m/z 378). At higher masses a small abundance of $Fe(C_{10}H_6)_5{}^+$ (at m/z 686) from the fifth dehydrochlorination step can be observed. A similar behavior was observed for the other halonaphthalenes. Scheme 1 shows the series of product ions produced in reactions 8−10 in the Fe^+/halonaphthalene systems.

Another primary reaction product was $M(C_{10}H_7X)^+$, which is a simple adduct complex ion. Isolation of $FeC_{10}H_7Cl^+$ resulted in the formation of $(C_{10}H_7)_2{}^+$ upon reactions with the neutral chloronaphthalene, either with the elimination of $FeCl_2$ or the entropy-favored elimination of Fe and Cl_2. Another reaction channel, shown in reaction 11, was observed for $n = 0-4$. Only

$$\mathrm{Fe(C_{10}H_7Cl)(C_{10}H_6)_{\mathit{n}}^+ + C_{10}H_7Cl \rightarrow Fe(C_{10}H_7Cl)(C_{10}H_6)_{\mathit{n}+1}^+ + HCl} \quad (11)$$

two steps analogous to reaction 11 could be observed for the Fe^+/iodonaphthalene system, and for that system these were the main reactions, excluding charge transfer reactions. An analogous behavior was observed in the phenyl halide study.[3] Fe^+ did not dehydroiodinate iodobenzene, whereas $FeC_6H_5I^+$ was observed to do so effectively. In the case of bromonaphthalene these reactions were all but absent, and in the case of fluoronaphthalene $Fe(C_{10}H_6)(C_{10}H_7F)^+$ was produced in another manner, that is from $Fe(C_{10}H_6)^+$ in an association reaction, and was unreactive with the neutral fluoronaphthalene.

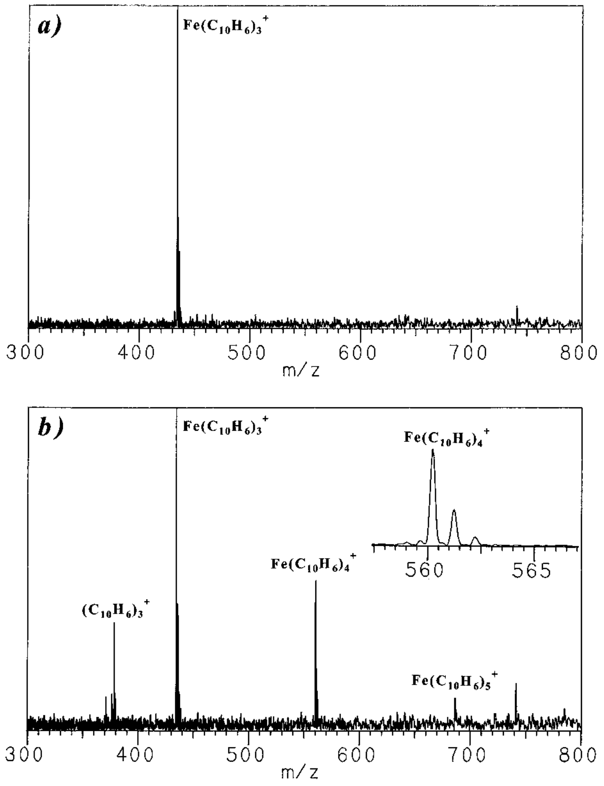
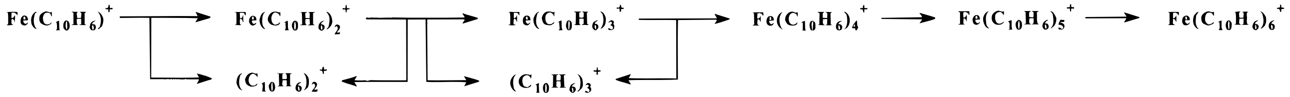


Figure 1. Mass spectra showing the reactions of $Fe(C_{10}H_6)_3{}^+$. (a) Mass spectrum obtained after a suitable reaction time of Fe^+ with chloronaphthalene and subsequent isolation of $Fe(C_{10}H_6)_3{}^+$ at m/z 434 using double-resonance techniques. (b) Mass spectrum obtained after the ion shown in (a) has been allowed to react with the neutral chloronaphthalene at a static pressure of 2×10^{-8} Torr for 5 s. The spectrum shows the reactant ion and the product ions from the reactions during this time interval. The insert shows well-resolved peaks for $Fe(C_{10}H_6)_4{}^+$ at m/z 560 and the ^{13}C isotope peaks at m/z 561 and 562 due to the ^{13}C abundance in the hydrocarbon ligand. The ion with m/z 740 is formed in association reactions and is not of interest to the reaction schemes discussed here.

The reactions of $MC_{10}H_6{}^+$ in the case of M = Sc, Ti, and V with the naphthalene halides were found to produce two common types of product ions, one according to reaction 8 and the other involving dehydrogena-

Scheme 1

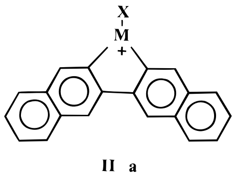


tion in conjunction with the dehydrohalogenation as shown in reaction 12.

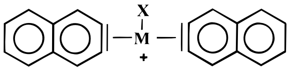
$$MC_{10}H_6{}^+ + C_{10}H_7X \rightarrow MC_{20}H_{10}{}^+ + [HX + H_2] \quad (12)$$

In the case of Sc^+ an ion with the formula $ScC_{20}H_{11}X^+$ ($X = F$, Cl, Br) was also observed, which then only involves the elimination of H_2 in the secondary reaction (reaction of $ScC_{10}H_6{}^+$ with the naphthalene halide). On the basis of the nature of the reactants, this ion possibly has two ligands and is then of the form $Sc(C_{10}H_6)(C_{10}H_5X)^+$. An analogous ion was observed for Ti^+ in the case of chloronaphthalene. Informative CID results could not be obtained for these two ionic species due to relatively low abundances of these ions.

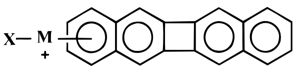
In the cases of Ti^+ and V^+ yet another reaction channel, and the dominant one, was observed to produce $M(C_{10}H_6)_2X^+$, which may be of the form shown in structures **IIa**−**c.** In most cases $M(C_{10}H_6)_2X^+$ was produced directly from $M(C_{10}H_6)^+$ in its reactions with the neutral naphthalene halide. As discussed below, however, in the case of V^+ and chloronaphthalene this ion could also be made by chlorine abstraction by $V(C_{10}H_6)_2{}^+$.



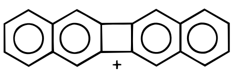
II a



II b



II c



III

Sc^+ has only two valence electrons and, thus, would not be expected to form an ion of the form shown in structures **IIa** but possibly one with structures **IIb** or **IIc**, assuming dative bonds between the metal and the naphthalyne ligands. No ion of this formula was observed in the case of Sc^+ with fluoronaphthalene, and for the other halides it was either missing or present in such low abundances that its existance could not be unambiguously verified. The formation of this ion involves the loss of a single hydrogen atom as was seen in the primary reaction of Ti^+ with the naphthalene halides. We propose **IIa** or **IIc** as the structure of $M(C_{10}H_6)_2X^+$ as it was found that MX was lost from this ion to form $(C_{10}H_6)_2{}^+$ (**III**) according to reaction 13. **IIa**

$$M(C_{10}H_6)_2X^+ \xrightarrow{[C_{10}H_7X]} (C_{10}H_6)_2{}^+ + MX \quad (13)$$

may be more likely in light of the fact that Sc^+ could form an ion of this formula with structure **IIc** but did not as stated above. $M(C_{10}H_6)_2X^+$ not only produced $(C_{10}H_6)_2{}^+$, as shown in reaction 13, but it was also established in the case of chloronaphthalene that $(C_{10}H_6)_3{}^+$ is produced directly in the reactions of this ion with the neutral chloronaphthalene (reaction 14) and not from $M(C_{10}H_6)_3Cl^+$, even though the latter ion was observed.

$$M(C_{10}H_6)_2Cl^+ + C_{10}H_7Cl \rightarrow (C_{10}H_6)_3{}^+ + [MCl + HCl] \quad (14)$$

Continuous ejection of an ion at *m/z* 497 ($Ti(C_{10}H_6)_2Cl{\cdot}C_{10}H_7Cl^+$) during the entire reaction time shows little or no reduction in the yield of the ion at *m/z* 378, $(C_{10}H_6)_3{}^+$. This means that the lifetime of the intermediate in the reaction of $Ti(C_{10}H_6)_2Cl^+$ with chloronaphthalene is shorter than the ejection time (on the order of a few microseconds) and probably involves a near simultaneous loss of TiCl and HCl.

The reactions of $Ti(C_{10}H_6)_2{}^+$ with the neutral chloronaphthalene produced only $Ti(C_{10}H_6)_3{}^+$, and neither of these two ions lost titanium to form the unmetalated oligomer ions $(C_{10}H_6)_2{}^+$ or $(C_{10}H_6)_3{}^+$. This is in contrast with the bahavior of Fe^+, described above, and also in contrast with the behavior of the related Ti^+/chlorobenzene system.[4]

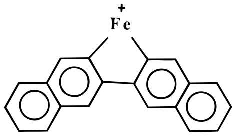
$V(C_{10}H_6)_2{}^+$ and $V(C_{10}H_6)_2Cl^+$ were product ions of the reactions of $V(C_{10}H_6)^+$ with chloronaphthalene. Unique compared with the other systems was the observation that $V(C_{10}H_6)_2{}^+$ was found to produce $V(C_{10}H_6)_2Cl^+$. The latter ion could lose VCl to produce $(C_{10}H_6)_2{}^+$, and $(C_{10}H_6)_3{}^+$ was also observed and produced in a manner analogous to the one described above for titanium. On the other hand and unlike the titanium case was the observation that $(C_{10}H_6)_2{}^+$ could also be produced from $V(C_{10}H_6)_2{}^+$ as was seen in case of Fe^+.

Some differences were observed for bromonaphthalene compared to chloronaphthalene aside from the ones listed in Tables 1 and 2. For example, $(C_{10}H_6)_2{}^+$ was only formed from $Fe(C_{10}H_6)^+$ and not from $Fe(C_{10}H_6)_2{}^+$ in the reactions of these ions with the neutral bromonaphthalene. Another example of different behavior was in the case of V^+, where $(C_{10}H_6)_2{}^+$ could only be produced from $V(C_{10}H_6)_2Br^+$ and not from $V(C_{10}H_6)_2{}^+$.

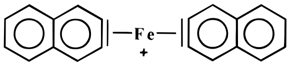
For the most part the reactions of bromonaphthalene were similar to those of chloronaphthalene, and most of the similarities and a few examples of different behavior have already been pointed out. Still, only four steps of dehydrobromination could be observed. The early transition metal ions (Sc^+, Ti^+, and V^+) showed similar reactivity toward fluoro-, chloro-, and bromonaphthalene, whereas Fe^+, Co^+, and Ni^+ were much less reactive toward fluoronaphthalene, and the latter two metal ions only participated in association reactions to form $M(C_{10}H_7F)^+$ and $M(C_{10}H_7F)_2{}^+$. The reactions of the metal ions with iodonaphthalene only resulted in one step of dehydroiodination (two steps in the case of Ni^+) and higher order reactions were of little interest.

It is clear from the discussion above that all of the metal ions behave differently in the reactions with the naphthalene halides, and there also are differences in the behavior of the halides. The reactions described above are the main reactions and those that could be characterized with certainty. Other higher order reaction products were observed in some cases but were not analyzed further because they were produced in low abundances.

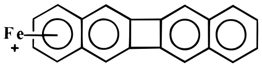
Structural and Thermodynamical Considerations. The structures of the complex ions produced in the second and higher order steps of the dehydrohalogenation are not obvious, but some clues can be found from their reactions and collision-induced dissociation studies. $Fe(C_{10}H_6)_2^+$ could possibly be of the form shown in the three structures, **IVa**−**c** (each structure can have several closely related isomers).



IV a

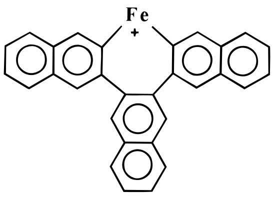


IV b

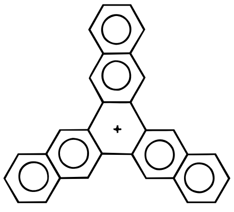


IV c

CID studies of $Fe(C_{10}H_6)_2^+$ with nitrogen as the collision gas showed only the formation of $(C_{10}H_6)_2^+$ through a loss of the iron atom. The CID results point to structure **IVa** or **IVc** as neither $Fe(C_{10}H_6)^+$ nor $(C_{10}H_6)^+$, which are logical fragments from structure **IVb**, was observed. CID studies of $Fe(C_{10}H_6)_3^+$ revealed the formation of $(C_{10}H_6)_3^+$, and the combined results, thus, show that both $(C_{10}H_6)_2$ and $(C_{10}H_6)_3$ have lower ionization potentials than iron (IP = 7.87 eV[23]). Possible structures for $Fe(C_{10}H_6)_3^+$ and $(C_{10}H_6)_3^+$, consistent with the experimental results and analogous to those reported for the related iron triphenylene complex ion and the triphenylene ion itself,[3,4] are presented in structures **Va**,**b**, respectively. Some support for these structures also come from the fact that 2,3-didehydronaphthalene is most stable, as discussed above.



V a



V b

CID on the metalated tetramer ions, such as $Fe(C_{10}H_6)_4^+$, failed to yield meaningful results, and in particular, the observation of the tetramer ion $(C_{10}H_6)_4^+$ could not be made.

Reaction 13 has the consequence that the ionization potential (IP) of $(C_{10}H_6)_2$ must be lower than that of either TiX or VX. Unfortunately, the IPs of these species have not been critically evaluated, so that a specific number cannot be assigned as the high value of the IP of $(C_{10}H_6)_2$ based on this observation. Furthermore, $Ti(C_{10}H_6)_3X^+$ was produced in abundances too small for obtaining desired CID results.

To the best of our knowledge, the heat of formation values for $C_{10}H_6$ and $C_{10}H_7$ have not been critically evaluated. In 1970, Grützmacher and Lohman[22] reported values for the heat of formation of four isomers of $C_{10}H_6$, 1,2-, 2,3-, 1,8-, and 1,5-didehydronaphthalene, to be 117, 91, 130, and 97 ± 15 kcal/mol, respectively. The study reported here utilized 1-halonaphthalenes, and therefore, formation of either 1,2- or 1,8-didehydronaphthalene ligands might be expected in the first step of the dehydrohalogenation. Rapid conversion to the more stable 2,3-didehydronaphthalene ligand may subsequently occur. Using 91 ± 15 kcal/mol as the heat of formation for the didehydronaphthalene ligand and heat of formation values for the bromonaphthalene, HBr, and Fe^+ from ref 23, the high limit for the value for the heat of formation of $FeC_{10}H_6^+$ can be calculated to be 332 kcal/mol and a low limit for the iron−ligand bond energy of 40 ± 15 kcal/mol can be deduced. This value is suspiciously low in comparison with the iron−benzyne bond energy (83 ± 3 kcal/mol[24]), suggesting that more accurate determinations of the heats of formation of didehydronaphthalenes are warranted or, what is less likely, that these reactions are that much more exothermic than the related phenyl halide reactions.

Pressure Dependence. Some pressure dependence was observed in the relative ratios of product ions formed in many of the higher order reactions. In some cases this pressure dependence was very significant, such that only at very low pressures could some of the higher mass ionic products be observed. An example of this behavior, and the one most carefully studied, was observed in the Fe^+/chloronaphthalene system. At the higher sample pressures, the formation of the larger ions is suppressed and the dimer ion, $(C_{10}H_6)_2^+$, dominates to a significantly greater extent than at the lower pressures. Figure 2 shows mass spectra obtained at two different pressures to illustrate this point. The spectrum in Figure 2a was obtained after a 2 s reaction time with the pressure of chloronaphthalene at 1.6×10^{-7} Torr, whereas the spectrum in Figure 2b was obtained after a 25 s reaction time with chloronaphthalene at 1.5×10^{-8} Torr. Among the high mass ions in the spectrum in Figure 2b are $Fe(C_{10}H_6)_n^+$ with $n = 3-5$, the last one, though, only in a small abundance at m/z 686. The spectra in Figure 1 show that the higher mass ions can only be observed in significant abundances at very low pressures. In fact, the highest mass ions could only be observed using an instrument equipped with cryo- and turbomolecular vacuum pumps that provided an extraordinarily clean and low background pressure and, thus, enabled studies of the reactions with the reactant gas at very low pressures (1×10^{-8} Torr). Even though these pressure conditions can be met using a diffusion-pumped instrument, the background in that case consists mainly of oils with which the metalated oligomer ions are very reactive, whereas the background in the cryo- and turbopumped instrument consisted mostly of gases that were relatively unreactive with the complex ions.

A similar effect has been observed in the related Fe^+/chlorobenzene case, and a report describing a detailed study of the pressure dependence of those reactions is emerging from our laboratory.[25] We assume that the pressure dependence of these two systems is similar in

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(24) The bond dissociation energy for $Fe^+-C_6H_4$ depends on the value for the heat of formation for C_6H_4. Measurements have given values ranging from 100 to 115 kcal/mol for this enthalpy. Thus, the bond dissociation energy for $Fe^+-C_6H_4$ has been given values in the literature ranging from 68 to 83 kcal/mol (see refs 2−6).

(25) Bjarnason, A.; Ridge, D. P. *J. Phys. Chem.* To be submitted for publication.

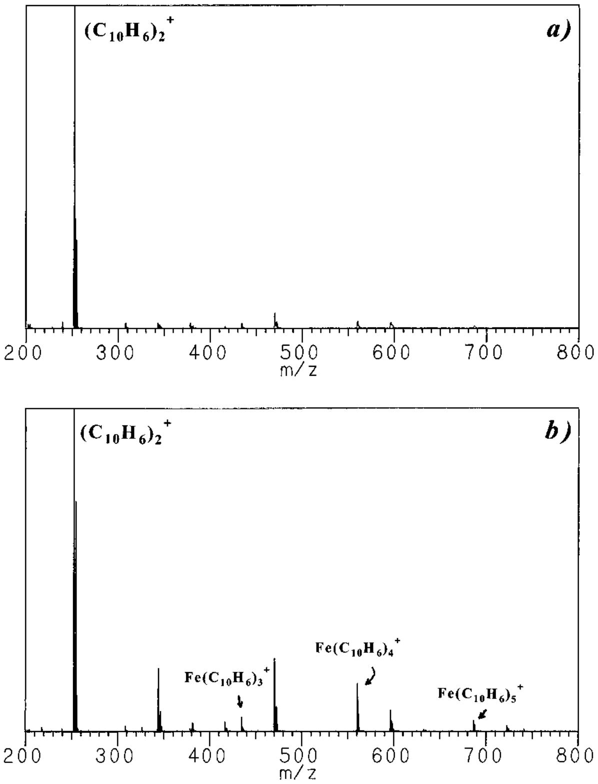

Figure 2. Mass spectra showing the effect of pressure on the relative yield of reaction product ions in the reactions of Fe^+ with chloronaphthalene. The spectrum in (a) was obtained after a 2 s reaction time with the pressure of chloronaphthalene at 1.6×10^{-7} Torr. The spectrum in (b) was obtained after a 25 s reaction time with the chloronaphthalene pressure at 1.5×10^{-8} Torr. Unlabeled peaks are due to ions produced in association reactions.

nature. Returning to the system described in the preceding paragraph, we attribute the pressure dependence of the reactions to the production of the *precursor* of the unmetalated dimer ion with considerable internal energy. For example, $Fe(C_{10}H_6)_2^+$ (**1**) can react to form the unmetalated dimer ion $(C_{10}H_6)_2^+$ (**2**), which terminates the reaction chain, or $Fe(C_{10}H_6)_3^+$ (**3**), which can then react on to form larger ions. **1** is formed with considerable internal energy (**1***), and the relative rates of the two main reaction channels to form **2** and **3** are heavily dependent on the amount of internal energy of **1***. **1*** can lose the excess internal energy by radiative relaxation,[26] and thus, at very low pressures (long time between collisions) we should see the branching ratio for the production of **2** and **3** representing the reactions of the relaxed **1**. The low-pressure behavior favors the formation of **3** compared to **2**, whereas the unrelaxed species **1*** favors the production of **2** over **3**. At higher pressure **1*** has not time to relax via a radiative process, and under these conditions the larger complex ions cannot be observed because **1*** predominantly produces **2**, which terminates the reaction chain that produces the larger complex ions.

One might argue if a collision gas would not serve the same purpose as ultra-low pressure in relaxing **1***, thereby enabling production and observation of the higher mass species. The study cited above[25] showed that intermediate complex ions in excited states can be effectively relaxed using a collision gas. A major problem, however, with the presence of a collision gas at high pressures for cooling purposes is that it favors the production of cluster species formed in association reactions, which again suppresses the formation of the desired high-mass species.

Conclusion

The results presented here only partially agree with the expected behavior deduced from the study of the related phenyl halides reported earlier.[3,4] Additional primary reaction channels were observed for the naphthalene halides, including a ring cleavage reaction by Sc^+ and a hydrogen atom elimination by Ti^+. The secondary and higher order reactions also deviated significantly from the phenyl halide reactions. In particular, the oligomer ion formation occured in some cases from different types of precursors than would have been expected from the phenyl halide study. Competitive reaction channels for species such as $Fe(C_{10}H_6)_n^+$, with $n = 1$ and 2, to either form the dimer ion $(C_{10}H_6)_2^+$ or to participate in further dehydrohalogenations to produce larger metalated oligomer ions were found to be highly pressure dependent. Only at ultra-low pressures could the largest ions be observed.

Each metal ion demonstrated reactivity different from the other ions, and each naphthalene halide exhibited unique behavior. The Fe^+/chloronaphthalene system was found to yield the largest complex ions, where up to six steps of dehydrochlorinations were observed. The metalated oligomer ions are postulated to have analogous structures to those put forth for the related metal–oligophenylene ions, in agreement with CID results.

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