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Reactions of First-Row Transition-Metal Ions (Sc^+–Zn^+) with Phenyl Halides in the Gas Phase

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Reported here are the reactions of the first-row transition-metal ions Sc^+–Zn^+ with phenyl halides studied in a Fourier transform mass spectrometer. This is an expansion of an earlier study concentrating on the reactions of Fe^+ with the same compounds. Six of the ten metal ions studied, Sc^+, Ti^+, V^+, Fe^+, Co^+, and Ni^+, were found to dehydrohalogenate at least some of the phenyl halides. Contrary to the previously reported behavior of Fe^+, oligomer ion formation of the form $(C_6H_4)_n{}^+$ from the corresponding metal complex ion $M(C_6H_4)_n{}^+$ could not be observed without kinetically exciting the complex ion in the case of M = Co, Ni. Oligomer ion formation could not be induced in the case of M = Sc, Ti, and V, presumably due to the low ionization potentials of these metals, as collision-induced dissociation of those complex ions ($M(C_6H_4)_n{}^+$) resulted in the formation of the metal ion rather than the oligomer ion. Cr^+, Mn^+, Cu^+, and Zn^+ were found to react differently or not at all with the phenyl halides; Zn^+ in particular, due to its high ionization potential, only participated in charge-transfer reactions. A lower limit for $D°(M^+–C_6H_4)$ was found to be 82 kcal/mol for M = Sc, Ti, V, and Ni, but 81 kcal/mol for M = Fe and Co. A high limit for the ionization potential of tetraphenylene was determined to be 7.86 eV.

Introduction

The reactions of Fe^+ with phenyl halides in the gas phase have been characterized[1-4] and were found to be of particular interest for two reasons. First, the iron–ligand bond energies $D°(Fe^+–C_6H_4)$ and $D°(Fe^+–C_6H_5)$ could be estimated. Second, the initial steps in the metal-catalyzed polymerization to produce polyphenylenes could be observed when oligomers of the form $(C_6H_4)_n{}^+$ were produced, with $n = 1–5$, from $Fe(C_6H_4)_n{}^+$, which in turn were formed in successive steps of dehydrohalogenations.

We now report a study of the reactions of the other first-row transition-metal ions (Sc^+–Zn^+) where considerable variations were observed in the behavior of the different metals. A comparison between the reactions of the different transition-metal ions is of both fundamental and practical interest, in part due to the catalytic properties of the metals and their uses as chemical ionization agents.[5] Aside from the studies of the reactions of Fe^+ with the phenyl halides mentioned above, Uppal and Staley[6] have reported three steps of dehydrochlorination in the reactions of Ti^+ with chlorobenzene, Jones and Staley have studied the reactions of Cu^+ with chlorobenzene,[7] and Stepnowski and Allison investigated the reactions of Ni^+ with chloro-, bromo-, and iodobenzene.[8]

Reactions of first-row transition-metal ions with alkyl halides have been reported by several researchers in addition to those mentioned above. This includes the studies of Allison and Ridge on the reactions of several metal ions with methyl iodide[9] and other alkyl halides,[10] and Armentrout and co-workers have studied the state-specific reactions of Fe^+ with methyl halides[11] and of Co^+ and Ni^+ with methyl halides.[12]

Table I. Primary Reactions of Sc^+–Zn^+ with Phenyl Halides

M	fluorobenzene	chlorobenzene	bromobenzene	iodobenzene
Sc^+	D^a ($n = 2$)	D ($n = 3$)	D ($n = 3$)	D ($n = 5$)
Ti^+	D ($n = 2$)	D ($n = 5$)	D ($n = 3$)	D ($n = 3$)
V^+	D ($n = 2$)	D ($n = 6$)	D ($n = 5$)	D ($n = 4$) $V(C_6H_5)^+ + I$
Cr^+	$Cr(C_6H_5F)^+$	$C_6H_5{}^+ + [CrCl]^b$	$C_6H_5{}^+ + [CrBr]^b$	$Cr(C_6H_5I)^+$
Mn^+	no reacn	no reacn	$C_6H_5{}^+ + [MnBr]^b$	$Mn(C_6H_5I)^+$
$Fe^{+\,c}$	D ($n = 2$)	D ($n = 7$)	D ($n = 7$)	$Fe(C_6H_5)^+ + I$
Co^+	$Co(C_6H_5F)^+$	$Co(C_6H_5Cl)^+$	D ($n = 6$)	$Co(C_6H_5)^+ + I$
Ni^+	$Ni(C_6H_5F)^+$	$Ni(C_6H_5Cl)^+$	D ($n = 6$)	D ($n = 5$) $Ni(C_6H_5)^+ + I$
Cu^+	$Cu(C_6H_5F)^+$ CT^d	$Cu(C_6H_5Cl)^+$ CT	$Cu(C_6H_5Br)^+$ CT	$Cu(C_6H_5I)^+$ CT
Zn^+	CT	CT $C_6H_5{}^+ + [ZnCl]^2$	CT $C_6H_5{}^+ + [ZnBr]^b$	CT $C_6H_5{}^+ + [ZnI]^2$

[a] Dehydrohalogenation: $M^+ + C_6H_5X \rightarrow M(C_6H_4)^+ + X$. n refers to the number of dehydrohalogenation steps observed (to form $M(C_6H_4)_n{}^+$). [b] Identity of neutral species not certain, but assumed to be the metal halide. [c] From ref 4. [d] Charge transfer: $M^+ + C_6H_5X \rightarrow C_6H_5X^+ + M$.

Experimental Section

The experimental approach has been described elsewhere,[4,5] but briefly, a Nicolet FTMS-2000 Fourier transform mass spectrometer with a 3.0-T superconducting magnet was used for these studies. Metal ions were made by focusing a laser pulse from a Tachisto Model 216 CO_2 laser onto a target of the pure metal (Sc, Ti, V, Cu, Zn) or stainless steel (Cr, Mn, Fe, Ni) placed on the direct insertion probe of the mass spectrometer.[13] Due to the

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ferromagnetism of cobalt, cobalt chloride was used instead of cobalt metal and the probe turned after each laser shot, so that the laser always struck a fresh spot on the thin film of cobalt salt deposited on the probe tip. The method of using laser ionization of salts instead of pure metals for study of metal ion reactions have been previously reported by Weil and Wilkins.[14] Following isolation of the metal ion, using double-ejection pulses, it was allowed to react with the sample molecule, which was incorporated through the batch inlet system and maintained at a static pressure of about 2×10^{-7} Torr. Reaction paths were elucidated by varying reaction times and verified by using double-resonance techniques.[15] Krypton or argon was used in most cases as a buffer gas to "cool" potentially "hot" metal ions and maintained at pressures 10 times that of the sample gas.

Reagents were commercially obtained and used without further purification, except for a few freeze–pump–thaw cycles.

Results and Discussion

The observed reactions are summarized in Table I. In short, the results were that Sc^+, Ti^+, V^+, Co^+, and Ni^+ were found to form $M(C_6H_4)_n{}^+$ in dehydrohalogenation reactions with the phenyl halides, each to a different extent (up to $n = 6$), depending on the metal and the halide. This behavior puts them in a group with Fe^+, but unlike the case of iron, there was no oligomer ion formation.[4] Speculative reaction mechanisms for these reactions have been reported[4] in the case of Fe^+ and are tentatively assumed to be the same for the other metal ions.

Cr^+, Mn^+, and Cu^+ were relatively unreactive toward the phenyl halides and at best formed metal–phenyl halide complex ions or formed $C_6H_5{}^+$ and MX. Zn^+, due to its high ionization potential, only participated in charge-transfer reactions with the phenyl halides.

Initially, two reaction channels are available, as pointed out by Ridge and co-workers:[1]

$$M^+ + C_6H_5X \rightarrow M(C_6H_4)^+ + HX \qquad (1)$$

$$M^+ + C_6H_5X \rightarrow M(C_6H_5)^+ + X \qquad (2)$$

The second reaction channel is never observed in the case of fluoro-, chloro-, or bromobenzene. Variations are observed in the case of iodobenzene. Sc^+ and Ti^+ only react with iodobenzene according to reaction 1, whereas Fe^+ and Co^+ only react via channel 2. V^+ and Ni^+ react through both channels.

Using known heat of formation values[16a] and calculations analogous to those reported for iron,[4] one can deduce that if metal ions undergo reaction 1 in the case of bromobenzene, then $D°(M^+–C_6H_4) > 81$ kcal/mol (M = Fe, Co). If the metals can undergo this reaction in the case of iodobenzene, then $D°(M^+–C_6H_4) > 82$ kcal/mol (M = Sc, Ti, V, Ni).[16b]

In addition, the formation of the phenyl cation ($C_6H_5{}^+$ + MX) was observed in the case of a few metal ions, whereas the formation of the phenyl radical and MX^+ was not observed, presumably due to the low ionization potential of the phenyl entity.

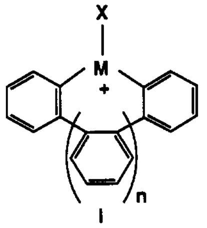
The discussion will now shift to describe the reactions of each transition metal, as none reacted in exactly the same manner as any of the others.

Sc^+. The main reaction product in the reactions of Sc^+ with fluorobenzene is $Sc(C_6H_4)^+$. This ion can react again with the neutral fluorobenzene to form $Sc(C_6H_4)_2{}^+$, but it can also react to form $C_6H_4F^+$ at m/z 95 (and probably $Sc(C_6H_5)$, which may be of the form $HSc(C_6H_4)$). The reactions of Sc^+ with chlorobenzene resulted in three steps of dehydrohalogenation to produce $Sc(C_6H_4)_n{}^+$ with n = 1–3. The last step was not efficient, as the production of $Sc(C_6H_4)_2(C_6H_5Cl)^+$ dominated. Three steps of dehydrohalogenation were also observed in the case of bromobenzene, although the third step is more efficient in this case. At the longest reaction time, $Sc(C_6H_4)_2(C_6H_5Br)^+$ and $Sc(C_6H_4)_3(C_6H_5Br)^+$ become the dominant ionic species present in the cell. Five steps of dehydrohalogenation were observed in the reactions of Sc^+ with iodobenzene and proceeded at near collision rates, whereas the reactions of the other halides were slower.

Sc^+ has only two valence electrons and several researchers have noted that this electron deficiency makes it one of the most reactive transition-metal ions.[17] It is, thus, not surprising to find that Sc^+ can dehydrohalogenate all of the phenyl halides and, in fact, Sc^+ has been found to be the only first-row transition-metal cation able to dehydrogenate benzene,[18] which points to the strength of the Sc^+–benzyne bond. The Sc^+–ligand bond strength may explain why fewer steps of dehydrohalogenation are observed in the case of Sc^+ compared to some of the other metal ions discussed below. If one assumes a mechanism for the formation of $Sc(C_6H_4)_n{}^+$ analogous to the one proposed for $Fe(C_6H_4)_n{}^{+,4}$ then each step involves the breaking of a M^+–C bond to add another benzyne unit to the complex ion. The relatively strong bond in the case of Sc may result in an earlier termination in this chain of reactions than for the other metals where this bond is weaker.

Ti^+. As in the case of Sc^+, dehydrohalogenation reactions were observed for all of the phenyl halides in their reactions with Ti^+. Five steps were observed in the case of chlorobenzene to finally form $Ti(C_6H_4)_5{}^+$, but fewer steps were observed with the other halides.

Two channels competed in the reactions of $Ti(C_6H_4)_n{}^+$ with $n > 1$ for all of the halides. These ions could either react in another step of dehydrohalogenation to produce $Ti(C_6H_4)_{n+1}{}^+$ or form $Ti(C_6H_4)_nX^+$. These latter ions were unreactive with the phenyl halide and may have structures according to I. Species of this type were also observed in the case of V^+ (see below), but not in the case of Sc^+. This may be explained by the fact that Sc^+ has only two valence electrons, both of which are bound to the phenyl groups and, thus, unlike Ti^+ and V^+ cannot form a bond to a halogen atom.



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Uppal and Staley,[6] using ion cyclotron resonance spectroscopy, found three steps of dehydrochlorination in the reactions of Ti^+ with chlorobenzene, in addition to a few

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other products, which were not investigated further.

V$^+$. Dehydrohalogenations were observed in the reactions of V$^+$ with all of the phenyl halides. Up to six steps were observed in the case of chlorobenzene, five for bromobenzene, four for iodobenzene, and two in the case of fluorobenzene. The initial reactions of V$^+$ with iodobenzene produce not only $\mathrm{V(C_6H_4)^+}$ but also $\mathrm{V(C_6H_5)^+}$ in a ratio of 1:1. Analogous to the case of Ti, $\mathrm{V(C_6H_4)_\mathit{n}^+}$ was found to form $\mathrm{V(C_6H_4)_\mathit{n}X^+}$, but in this case, not for all values of $n > 1$ ($\mathrm{X} = \mathrm{F}$ or I, $n = 2$; X = Cl, $n = 2$–4; X = Br, $n = 2$–5). Because V$^+$ has one valence electron more than Ti$^+$, one might ask why the formation of $\mathrm{V(C_6H_4)_\mathit{n}X_2^+}$ (from $\mathrm{V(C_6H_4)_\mathit{n}X^+}$) was not observed. Several reasons could be formulated, one of which could be steric hindrance (not in the final product, but rather in the intermediate $[\mathrm{(C_6H_4)_\mathit{n}(X)V{-}XC_6H_5}]^+$), but further discussion of this point would be highly speculative.

Cr$^+$. Cr$^+$ was found to be relatively unreactive toward the phenyl halides. The reactions with fluorobenzene only yielded $\mathrm{Cr(C_6H_5F)^+}$ and $\mathrm{Cr(C_6H_5F)_2^+}$ at very long reaction times. In the case of chlorobenzene only $\mathrm{(C_6H_5)_2^+}$ was observed, which presumably was produced in self chemical ionization of chlorobenzene molecular ions (produced in small amounts in charge-exchange reactions with Cr$^+$) with the neutral chlorobenzene. The same ion was observed in the case of bromobenzene, but in this case, it was produced from $\mathrm{C_6H_5^+}$, which in turn was formed in the reactions of Cr$^+$ with bromobenzene. $\mathrm{Cr(C_6H_5I)^+}$ was produced in the reactions with iodobenzene, and this ion reacts further to form $\mathrm{Cr(C_6H_5I)(C_6H_5)^+}$. The unreactive nature of gas-phase Cr$^+$ has been noted by several researchers.[19] Ground-state Cr$^+$ has the relatively stable half-filled 3d^5 electron configuration, and its reactions, therefore, tend to be more endothermic than those of the other first-row transition-metal ions. It cannot be ruled out that the small abundance of reaction products, described above for these reactions, was produced by Cr$^+$ in excited states, which may have been present in low abundances. Despite the generally unreactive nature of gas-phase chromium, Schwarz and co-workers have characterized a variety of products in the reactions of Cr$^+$ with 4-octyne.[20] Georgiadis and Armentrout have recently studied the reactions of ground-state Cr$^+$ with methane.[19d] Confirming the observations of others,[19] that no exothermic reaction channels are possible, they were able to detect and characterize several *endothermic* reaction channels in addition to the previously known one.

Mn$^+$. Mn$^+$, with the ground-state configuration 3d^{5}4s^1, was realatively unreactive toward the phenyl halides. No reactions were observed in the case of fluorobenzene and chlorobenzene. The reactions of Mn$^+$ with bromobenzene and iodobenzene were analogous to those of Cr$^+$ described above. The unreactive nature of Mn$^+$ in the gas phase has been discussed by several researchers, and a few have suggested explanations of this phenomenon.[21] It should be noted, however, that Schwarz and co-workers have observed unexpectedly rich chemistry in the reactions of Mn$^+$ with 4-octyne.[20b,22]

Fe$^+$. The reactions of Fe$^+$ with the phenyl halides have been described elsewhere,[4] so only a brief account will be given here. Dehydrohalogenation was observed in all cases save iodobenzene, with complex ions of the form $\mathrm{Fe(C_6H_4)_\mathit{n}^+}$ being produced with $n = 1, 2$ in the case of fluorobenzene and $n = 1$–7 in the cases of chlorobenzene and bromobenzene. The complex ions with $n > 1$ can lose the iron atom to form oligophenylene ions of the form $\mathrm{(C_6H_4)_\mathit{n}^+}$ with $n = 2$–5. This implies that the ionization potential of these oligophenylene units are lower than that of iron. $\mathrm{Fe(C_6H_5)^+}$ was the initial product in the reactions of iodobenzene. This ion reacted again with neutral iodobenzene to form $\mathrm{Fe(C_6H_5)_2^+}$, which in turn reacted in two successive dehydroiodination reactions with iodobenzene to form $\mathrm{Fe(C_6H_5)_2(C_6H_4)_\mathit{n}^+}$ with $n = 1, 2$. $D^\circ(\mathrm{Fe^+{-}C_6H_4}) > 81$ kcal/mol has been previously reported.[4] Huang and Freiser[3] report a high limit of 86 kcal/mol for this bond energy.

Co$^+$. Co$^+$ was found to dehydrohalogenate only bromobenzene. Six steps of dehydrobromination were observed, but despite a number of similarities between iron and cobalt (such as having IP differing of only 0.01 eV), the oligophenylene ion production was not observed, except by collision-induced dissociation (see below). The reactions of Co$^+$ with fluorobenzene and chlorobenzene only resulted in the formation of $\mathrm{Co(C_6H_5X)_\mathit{n}^+}$ with $n = 1, 2$. The reactions of Co$^+$ with iodobenzene were analogous to those of iron. $\mathrm{Co(C_6H_5)^+}$ is the initial product and reacts again to form $\mathrm{Co(C_6H_5)_2^+}$. This ion can dehydroiodinate the iodobenzene three times in succession to form $\mathrm{Co(C_6H_5)_2(C_6H_4)_\mathit{n}^+}$ with $n = 1$–3.

Ni$^+$. The reactions of Ni$^+$ with fluorobenzene and chlorobenzene produced only $\mathrm{Ni(C_6H_5X)_\mathit{n}^+}$ with $n = 1, 2$. The other phenyl halides underwent dehydrohalogenation reactions. Six steps were observed in the case of bromobenzene, and five in the case of iodobenzene. Iodobenzene was also found to produce $\mathrm{Ni(C_6H_5)^+}$ in addition to $\mathrm{Ni(C_6H_4)^+}$ in the primary reactions with Ni$^+$ in a ratio of 7:3, respectively. Stepnowski and Allison[8] studied the initial (primary) reaction of Ni$^+$ with chloro-, bromo-, and iodobenzene. They found Ni$^+$ to dehydrohalogenate bromobenzene and observed the same primary reaction in the case of iodobenzene but found a ratio of 55:45 in the products $\mathrm{Ni(C_6H_5)^+}$ and $\mathrm{Ni(C_6H_4)^+}$, respectively. They found no reaction in the case of chlorobenzene. As the dehydrohalogenation of chlorobenzene has to be exothermic, because it is so in the case of bromobenzene, they conclude that the initial insertion of Ni$^+$ into the C–Cl bond does not occur. It should be noted that dehydrochlorination of chlorobenzene by Ni$^+$ could be observed in the study reported here, when no buffer gas was present, and is presumably due to "hot" nickel ions.

Cu$^+$. The ground state of Cu$^+$ has a filled shell (3d^{10}), and it is, thus, not surprising that this metal ion has been found to be relatively stable and unreactive. The only products observed in the reactions of Cu$^+$ with the phenyl halides were condensation complexes of the form $\mathrm{Cu(C_6H_5X)^+}$ and $\mathrm{Cu(C_6H_5X)_2^+}$. In the case of bromobenzene and iodobenzene an ion is observed at m/z 154, corresponding to $\mathrm{(C_6H_5)_2^+}$. This ion is produced by the reactions of the phenyl halide molecular ion (produced in charge-exchange reactions of the phenyl halide with the copper ions) with the neutral phenyl halide. This was confirmed by self chemical ionization experiments with the

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phenyl halides. Jones and Staley[7] observed the same types of products in their investigation of the reactions of Cu^+ with chlorobenzene. They also detected chlorobenzene molecular ions in extraordinary yields and concluded that "hot" copper ions participated in collisional ionization of the chlorobenzene.

Zn^+. Zn^+, due to its high ionization potential, reacts with fluorobenzene only through charge-transfer reactions to produce $C_6H_5F^+$. Charge-transfer reactions to produce the phenyl halide molecular ion also dominate in the case of chlorobenzene, bromobenzene, and iodobenzene, but the formation of $C_6H_5^+$ is also observed with the elimination of ZnX. No complex ions of the form $Zn(C_6H_5X)^+$ were observed.

Collision-Induced Dissociation. Collision-induced dissociation (CID) was performed on several of the reaction products in order to gain more information about the nature of the ligands and to bracket the ionization potentials of the oligophenylenes. Ionization potentials (IP) for bi- and triphenylene have been critically evaluated[16] and found to be 7.56 and 7.84 eV, respectively. These are lower than that of iron (7.870 eV[7]), and hence these oligophenylenes retain the charge when the iron is lost from the iron oligophenylene complex ions. Tetraphenylene must likewise have a lower ionization potential than iron, as it also retains the charge when the iron is lost from the iron tetraphenylene complex ion. The pentaphenylene ion is a special case, as it could not easily be formed upon CID from the iron pentaphenylene complex ion. It is not clear wheather the mechanism for its formation involves simple loss of Fe or if it is produced directly in the reactions of the iron tetraphenylene complex ions with the neutral phenyl halide. Thus, it is not certain if pentaphenylene has a lower IP than iron. Hexa- and heptaphenylene ions could not be produced from the corresponding irons complexes, but it should be noted that the complex ions were only produced in small abundances (particularly the iron heptaphenylene complex ion) making CID studies difficult.

Cobalt has an IP of 7.86 eV,[16] only 0.01 eV lower than that of iron. The oligomer formation was never observed from the cobalt oligophenylene complex ions, but $(C_6H_4)_n^+$ with $n = 2$–4 could be produced upon CID of the corresponding cobalt complex ions ($Co(C_6H_4)_n^+$). The product ions, thus, must have an IP lower than that of cobalt. CID studies of the cobalt pentaphenylene complex ions did not result in the production of the pentaphenylene ion or cobalt ions, but as in the case of the analogous iron complex ion, other products could be forced to form in processes that are not fully understood.

Nickel has an IP of 7.635 eV,[16] and $Ni(C_6H_4)_2^+$ could be forced to lose Ni upon CID and produce $(C_6H_4)_2^+$, as was expected because of the lower ionization potential of $(C_6H_4)_2$, whereas the larger complex ions lost Ni^+. The analogous complex ions of scandium, titanium, and vanadium all lose the metal ion upon CID, due to their low ionization potentials (6.54, 6.82, and 6.74 eV, respectively[16]). This, however, points to a structure analogous to those reported for the iron complexes,[4] as opposed to other possible structures, such as of the form L–M^+–L, where a loss of one ligand (one phenylene unit) would be expected.

Conclusions

The study reported here is an effort to extend the scope of a previous report,[4] that is, to cast light on the fundamental mechanisms of the polymerization of phenylene and to investigate the different behavior of transition-metal ions in their reactions with the phenyl halides. Oligophenylenes are most readily produced in the reactions of the iron cation with chloro- and bromobenzene. Several transition-metal ions can induce dehydrohalogenation in all of the phenyl halides, whereas others, in particular Co^+ and Ni^+, can react in this manner only with bromobenzene. It appears that the carbon–halogen bond strength is of fundamental importance in this respect. The dehydrohalogenation of chlorobenzene by Co^+ and Ni^+ should be more favorable (exothermic) than that of bromobenzene. The experimental facts presented here must point to a less favorable initial insertion of the metal ion into the stronger (than C–Br) C–Cl bond. It is of interest to note that only two steps of dehydrohalogenation could be observed in the case of fluorobenzene, whereas all the other phenyl halides participated in several additional steps in their reactions with at least some of the transition-metal ions. This also supports the speculations above that the carbon–halogen bond strength is of no less importance than the question of exothermicity of the overall reaction, in determining wheather a reaction occurs or not.

From the CID experiments it is clear that the IP of tetraphenylene is lower than that of iron (7.87 eV) and that of cobalt (7.86 eV). The investigation of other polymerization systems is in progress as well as a study of the reactions of second- and third-row transition-metal ions.

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