Gas Phase Ion Molecule Reactions of η^6-Arenetricarbonylchromium Compounds with Propene, Benzene and Toluene

G. CETINI, O. GAMBINO, P. MICHELIN LAUSAROT, L. OPERTI, G. A. VAGLIO*, M. VALLE and P. VOLPE

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Turin, Italy

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Abstract

Positive chemical ionization mass spectra of arenetricarbonylchromium compounds with propene, benzene and toluene, at about 0.5 torr, are reported. Protonation, charge exchange, fragmentation and CO substitution processes occur for all these complexes. The abundances of the $[M + H]^+$ and substituted ions strongly depend on the reagent gas and, for any given gas, on the coordinated arene. The effects of the nature of the reagent gas and of the coordinated arene on the ion abundances are discussed and reaction mechanisms suggested.

Introduction

Recently an increasing number of studies on gas phase reactions between metal-containing ions and small organic molecules have been reported. Although ion cyclotron resonance spectrometry [1–5], Fourier transform mass spectrometry [6–8] and ion beam techniques [9, 10] are the best methods to investigate the gas phase reactivity and obtain information about ionic bond energies and reaction mechanisms, conventional chemical ionization mass spectrometry can give an overall picture of the gas phase behaviour [8, 11, 12]. By comparing these results with the behaviour exhibited in solution the effect of the environment and in particular of the solvent can be elucidated [13].

In previous papers we have described the gas-phase ion/molecule reactions of some classes of mono- and bi-metal carbonyls with different reagent gases [8, 11–13]. Here we report the results obtained by the positive ion chemical ionization mass spectra (CIMS) of (η^6-Arene)$Cr(CO)_3$ complexes where Arene = $C_6H_5COCH_3$ **1**, $C_6H_5COC_2H_5$ **2**, $C_6H_5COC_3H_7$ **3**, $C_6H_5COOCH_3$ **4**, 1,3,5-$(CH_3)_3C_6H_3$ **5**, $CH_3C_6H_5$ **6**, with propene, benzene and toluene at about 0.5 torr as reagent gases.

Experimental

All the compounds were prepared according to the literature [14].

The mass spectra were run on a double-focusing MS80 mass spectrometer of the Laboratory of Gas Chromatography-Mass Spectrometry, University of Turin.

Operating conditions were: primary electron energy 50 eV, emission current 500 μA, accelerating voltage 4 kV, resolution 1000 (10% valley definition), scan rate 3 s/dec.

TABLE I. Abundances of the Most Significant Ions in the CIMS of (η^6-Arene)$Cr(CO)_3$ Compounds with Propene (P) at 0.5 torr.[a]

Arene	Ions					
	$[M+H]^+$	$[M]^+$	$[M-CO]^+$	$[M-2CO]^+$	$[M-3CO]^+$	$[M-3CO+P]^+$
$C_6H_5COCH_3$	93	100	–	2	7	31
$C_6H_5COC_2H_5$	89	100	–	6	8	34
$C_6H_5COC_3H_7$	78	100	–	5	12	32
$C_6H_5COOCH_3$	35	100	–	6	23	15
1,3,5-$(CH_3)_3C_6H_3$	22	100	3	1	6	7
$C_6H_5CH_3$	26	100	3	1	3	8

[a] Ion abundances corrected for natural isotopic contribution.

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*Author to whom correspondence should be addressed.

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The samples were introduced through an all-glass inlet system or through a direct insertion probe according to their volatility. Propene was introduced through an automatic multiple reagent gas inlet system; benzene and toluene (distilled prior to use) were introduced through an evacuated glass line connected to the ion source by a micrometer valve.

Results and Discussion

In Table I the abundances of the most significant ions in the CIMS of (η^6-Arene)Cr(CO)$_3$ compounds with propene at about 0.5 torr are reported.

Beside the processes of protonation, charge exchange and fragmentation, which are usually observed in chemical ionization mass spectrometry, substitution reactions of carbonyl groups with propene take place.

The (η^6-Arene)Cr(CO)$_3$ compounds have a proton affinity higher than that of isobutane (195 kcal mol^{-1}), because they display $[M + H]^+$ ions, which are the base peak in the CIMS with isobutane. The proton affinity of propene (182 kcal mol^{-1} [15]) is lower than that of isobutane and this explains the fact that the CIMS of all the compounds here studied (Table I) exhibit protonated molecules, the abundances of which depend on the nature of the coordinated ligand.

We have carried out experiments at a reduced pressure of propene and have observed that the abundances of $[C_3H_7]^+$ and $[C_4H_7]^+$, originated by the reagent gas, decrease respectively in the presence and increase in the absence of the samples. $[C_3H_7]^+$ and $[C_4H_7]^+$ are, therefore, the ions mainly involved in the protonation process occurring in the ion source with propene, as in the case of (Alkyne)Co$_2$(CO)$_6$ compounds [12].

It has been suggested that the gas-phase protonation of the (η^6-Arene)Cr(CO)$_3$ compounds takes place on the ligand, when an appropriate functional group is present, such as the carbonyl group in **1**, **2**, **3** and the methoxy group in **4**. On the contrary, the site for the proton addition is considered to be the chromium atom in the case of **5** and **6** containing mesitylene or toluene as ligand [11].

The different protonation site is likely to be responsible for the strong dependence of the $[M + H]^+$ ion abundances on the nature of the coordinated arene. In fact, these abundances range from 40% (phenylketones as ligands) to 16% (hydrocarbons as ligands) of the total ion current transported by the metal-containing ions.

From the data reported in Table I it appears that the (η^6-Arene)Cr(CO)$_3$ compounds, in the presence of propene at about 0.5 torr, give $[M - 3CO + P]^+$ (P = propene) ions, in which the carbonyl groups are substituted by a propene molecule. The abundances of these substituted ions strongly depend on the nature of the coordinated ligand. Trends can be correlated with the metal–CO bond strength, which increases going from **1**, **2** and **3** (phenylketones as ligands) to **5** and **6** (hydrocarbons as ligands) [16]. Data of Table I show an intermediate behaviour of **4**, where arene is methylbenzoate. The chromium–CO bond strength of **4** is very similar to that of **1** and therefore the metal–CO bond strength is not the only factor affecting formation and stability of the $[M - 3CO + P]^+$ ions.

When benzene is introduced into the ion source of the mass spectrometer at a pressure of about 0.5 torr, with the (η^6-Arene)Cr(CO)$_3$ compounds the overall behaviour is analogous to that described above and the ions are originated by protonation, charge exchange, fragmentation and CO substitution processes. However, the data of Table II show that the relative abundances of $[M + H]^+$ and $[M - 3CO + B]^+$ (B = benzene) ions are very different from the corresponding ions formed in the presence of propene. The $[M + H]^+$ ions are weak in the CIMS of all these complexes, and they are even weaker when the coordinated arene is a hydrocarbon (**5** and **6**).

The proton affinity of benzene (178.0 kcal mol^{-1} [17]) is lower than that of isobutane and, therefore, it is lower than that of all these (η^6-Arene)Cr(CO)$_3$ compounds. As shown in Table II, the protonated

TABLE II. Abundances of the Most Significant Ions in the CIMS of (η^6-Arene)Cr(CO)$_3$ Compounds with Benzene (B) at 0.5 torr[a].

Arene	Ions					
	$[M + H]^+$	$[M]^+$	$[M - CO]^+$	$[M - 2CO]^+$	$[M - 3 CO]^+$	$[M - 3CO + B]^+$
$C_6H_5COCH_3$	10	76	1	13	4	100
$C_6H_5COC_2H_5$	8	50	–	23	13	100
$C_6H_5COOCH_3$	6	100	1	15	8	57
1,3,5-$(CH_3)_3C_6H_3$	6	100	12	13	7	37
$C_6H_5CH_3$	7	100	19	6	2	33

[a] Ion abundances corrected for natural isotopic contribution.

TABLE III. Abundances of the Most Significant Ions in the CIMS of (η^6-Arene)Cr(CO)$_3$ Compounds with Toluene (T) at 0.5 torr.[a]

Arene	Ions					
	$[M+H]^+$	$[M]^+$	$[M-CO]^+$	$[M-2CO]^+$	$[M-3CO]^+$	$[M-3CO+T]^+$
$C_6H_5COC_2H_5$	6	100	1	11	9	42
$C_6H_5COC_3H_7$	9	100	1	9	8	44
$C_6H_5COOCH_3$	5	100	–	2	4	12
1,3,5-$(CH_3)_3C_6H_3$	3	100	8	2	4	9
$C_6H_5CH_3$	4	100	5	–	4	11

[a] Ion abundances corrected for natural isotopic contribution.

molecules are always formed in the presence of benzene, but their abundances are low because in the CI mass spectrum of benzene alone at about 0.5 torr more than 90% of the ion current is transported by $[C_6H_6]^+$, which is not prone to behave as a Lewis acid.

The substituted $[M - 3CO + B]^+$ (B = benzene) ions display very strong abundances and transport about 50% of the total ion current when arene is a phenylketone as in **1** and **2**. This suggests that the substitution process is strongly exothermic and can be related to the nature of the entering ligand, which is a 6-electron donor and gives substitution ions with a krypton valence shell configuration.

Also Cr(CO)$_6$ reacts in the ion source with benzene at about 0.5 torr to give $[Cr(CO)_3B]^+$ and $[CrB_2]^+$.

In the presence of toluene at about 0.5 torr the (η^6-Arene)Cr(CO)$_3$ compounds give protonated molecules and $[M - 3CO + T]^+$ (T = toluene) substituted ions, which transport about 25% of the total ion current, when arene is a phenylketone as in the case of **2** and **3** (Table III). The $[M + H]^+$ ions display rather low abundances and this can be related to the very weak ions, which are able to donate protons in the toluene plasma. The $[M - 3CO + T]^+$ ions transport a lower percentage of the total ion current than do the $[M - 3CO + B]^+$ ions and, therefore, the presence of a methyl substituent on the benzene ring is by itself sufficient to halve their relative abundances likely for steric reasons.

Within the typical residence time in a CI ion source (10^{-4}–10^{-3} s) the (η^6-Arene)Cr(CO)$_3$ compounds give substituted ions in which all the carbonyl groups are replaced by propene, benzene or toluene, but neither detection of $[M - CO + L]^+$ and $[M - 2CO + L]^+$ ions (L = propene, benzene, toluene) takes place nor does replacement of the coordinated arene occur.

On the basis of the results on the Cr(CO)$_6$/NH$_3$ and Mo(CO)$_6$/NH$_3$ systems obtained by FT–ICR experiments [8] it can be suggested that the absence of the $[M - CO + L]^+$ ions indicates that $[(\eta^6\text{-Arene})Cr(CO)_3]^+$ ions are inert, like $[Cr(CO)_6]^+$ and $[Mo(CO)_6]^+$.

The $[(\eta^6\text{-Arene})Cr(CO)_2]^+$ ions probably do not play a significant role in the substitution processes, as their abundances are very low under CI conditions [11]. Therefore the observed $[(\eta^6\text{-Arene})CrL]^+$ ions are mainly originated according to the reaction:

$$[(\eta^6\text{-Arene})Cr(CO)]^+ + L \longrightarrow [(\eta^6\text{-Arene})CrL]^+ + CO$$

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