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ION–MOLECULE CONDENSATION REACTIONS IN THE MASS SPECTRA OF ARENECHROMIUM TRICARBONYL DERIVATIVES

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SUMMARY

The reactions of substituted arenechromium tricarbonyl derivatives in a mass spectrometer source have been studied, and the existence of secondary ions of the types $[Ar_2Cr_2(CO)_3]^+$ and $[Ar_2Cr_3(CO)_6]^+$ confirmed. Such ions are shown to arise from ion–molecule reactions at pressures of 5×10^{-6} to 2×10^{-5} mmHg. Appearance potentials have been measured and used to confirm the reactant ions, and also to provide information on the fragmentation pathways of the secondary ions.

We have previously reported[1] the occurrence of binuclear ions of the type $[Ar_2Cr_2(CO)_n]^+$ where $n=0, 1, 2, 3$ in the mass spectra of the compounds $ArCr(CO)_3$ where Ar = toluene, mesitylene or methyl benzoate. It was shown that these ions were produced by ion–molecule reactions of the general type

$$ArCr(CO)_3 + [ArCr(CO)_m]^+ \longrightarrow [Ar_2Cr_2(CO)_n]^+ + (m-n)\,CO$$

and that by introducing two physically separated compounds into the mass spectrometer, mixed ligand ions of the general formula $[ArAr'Cr_2(CO)_n]^+$ could be produced. Other work[2-4] suggests that such ion–molecule reactions are of general occurrence for organo-transition metal derivatives in the gas phase. In this work we have extended the study of ion–molecule reactions to nine arenechromium tricarbonyls and have observed both binuclear and trinuclear ions in all cases. We report also on the fragmentation pathways and energetics of decomposition of these secondary ions.

In most conventional mass spectrometers, ions formed by electron impact are removed from inside the ion-source by a small applied electric field (the repeller potential) and hence have a residence time of only 10^{-6}–10^{-7} seconds. At normal operating pressures ($\approx 10^{-6}$ mmHg) most organic ions are unable to undergo collision whereas at only moderately higher pressures many organometallic ions give rise to ion–molecule reactions presumably because of their larger reaction cross-section. In mass spectroscopic studies of such reactions three types of approach are usually employed:

(*a*) variation of ion-intensity with ion-repeller voltage,
(*b*) variation of ion-intensity with pressure,
(*c*) measurement of appearance potentials.

TABLE 1

APPEARANCE POTENTIALS (eV) FOR THE SYSTEM $[Ar_2Cr_2(CO)_3]^+$

Parent Compound	$[Ar_2Cr_2(CO)_3]^+$	$[Ar_2Cr_2(CO)_2]^+$	$[Ar_2Cr_2]^+$	$[Ar_1Cr_2(CO)_3]^+$	$[Ar_1Cr_2(CO)_2]^+$	$[Ar_2Cr]^+$	$[Ar_2Cr_3(CO)_6]^+$	$[ArCr(CO)_3]^+$
$(CH_3)_6C_6Cr(CO)_3$	6.55	8.40	10.00	8.92	10.30	7.51	6.72	6.35
$NH_2C_6H_5Cr(CO)_3$	6.49	8.52	9.82	8.89	11.02	6.93		6.52
$(CH_3)_3C_6H_3Cr(CO)_3$	6.60	9.38	9.75	9.28	11.27	7.15		6.60
$(CH_3)_2C_6H_4Cr(CO)_3$	6.68	9.42	10.01	9.26	10.27	7.21		6.70
$CH_3OC_6H_5Cr(CO)_3$	6.70	9.35	10.05	9.10	10.31	7.10		6.75
$CH_3C_6H_5Cr(CO)_3$	7.16	9.20	10.60	9.68	11.80	7.51		6.69
$C_6H_6Cr(CO)_3$	6.54		10.11	9.28	10.21	7.34	6.95	6.74
$ClC_6H_5Cr(CO)_3$	6.95		10.15	9.00	10.07			7.00
$COOCH_3C_6H_5Cr(CO)_3$	6.81	8.30	9.12			7.32	7.30	7.02

We have carried out each of these measurements on the arenechromium tricarbonyl system and summarise our findings as follows:

(a). Variation of ion-intensity with ion-repeller voltage

It has been shown that[5] the ratio of primary to secondary ions produced in an ion-molecule reaction may be expressed by the equation:

$$\frac{i_s}{i_p} = n_2 \cdot l \cdot \left(\frac{4\pi^2 \cdot e^2 \cdot \alpha}{\mu}\right)^{\frac{1}{2}} \cdot \left(\frac{2m_1}{e \cdot E \cdot l}\right)^{\frac{1}{2}} \cdot \eta$$

where

n_2 = concentration of unionized gas in the ion chamber
l = average ion path length in the ion-source
e = electronic charge
α = polarisability of the molecule
μ = reduced mass of reactants
m_1 = mass of the reactant ion
η = probability that a collision will lead to reaction
E = ion repeller electric field

Hence provided that l does not change with E a plot of i_s/i_p against $1/\sqrt{E}$ should give a linear relationship. In the case of benzene-, mesitylene- and (methyl benzoate)chromium tricarbonyls, the compounds examined in this respect, we do in fact observe this relationship (Fig. 1).

(b). Variation of ion-intensity with pressure

The intensity of a secondary ion will increase with the square of the pressure while that for a primary ion will increase linearly. Hence the ratio of the intensities of the primary to secondary ions should also increase linearly with pressure.

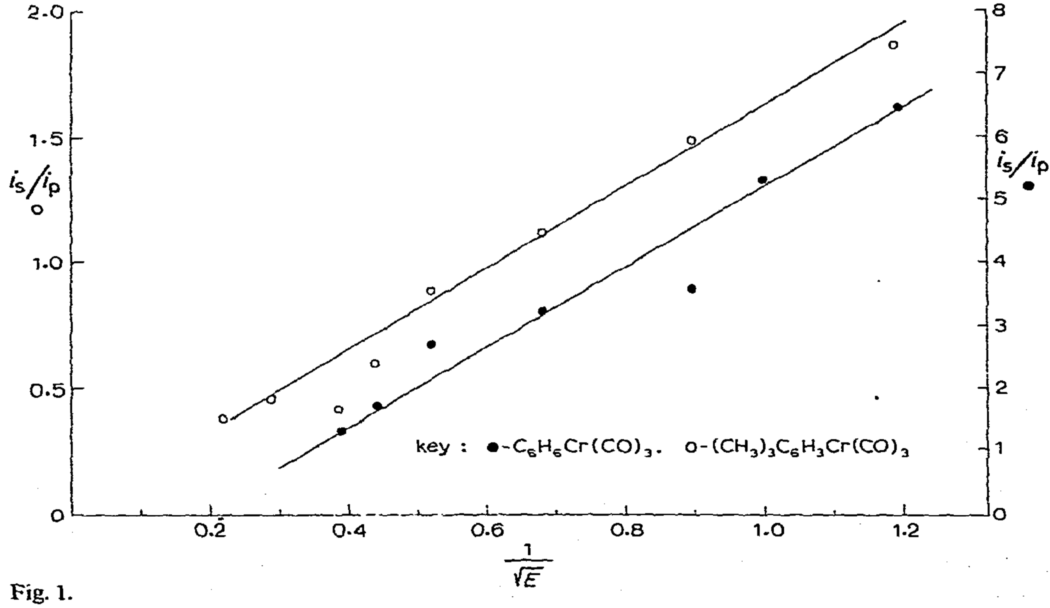


Fig. 1.

In all cases this relationship is observed. We have not been able to measure accurately the intensities for the entire range of compounds in the case of the trinuclear cations but where it was possible the ratio of intensities for trinuclear to dinuclear ions is also linear. A plot of log i_s against log i_p should yield a slope of value 2 and in all cases measured this is seen to lie between 1.92 and 2.06. Similarly log i_t (i_t = intensity of trinuclear peak) against log i_s should yield a slope of 1.5 and we observe values of 1.46–1.51.

(c). *Measurement of appearance potentials*

The above results show that the formation of the binuclear cations is due to ion–molecule collisions and not molecule–molecule collisions followed by ionisation. This fact having been established, the identity of the reactant ion has been determined by measurement of the appearance potentials of the secondary ions. The primary ion whose appearance or ionisation potential most closely corresponds to that of the product ion is generally considered to be the reactant ion allowing that certain assumptions are made regarding the endothermicity of the reaction[6,7].

From these measurements (Table 1) we have shown the reaction to be:

$$\mathrm{ArCr(CO)_3 + [ArCr(CO)_3]^+ \rightarrow [Ar_2Cr_2(CO)_3]^+ + 3\,CO}$$

It has not been possible in many cases to measure the appearance potentials of the parent trinuclear ions but in the cases of mesitylene- and benzenechromium tricarbonyls we report the reaction as:

$$\mathrm{[Ar_2Cr_2(CO)_3]^+ + ArCr(CO)_3 \rightarrow [Ar_2Cr_3(CO)_6]^+ + Ar}$$

One further piece of evidence to establish these reactions as being due to ion–molecule collisions is given by the plot of the ratio of intensities for binuclear to parent ions against energy of the bombarding electrons (Fig. 2) at a single pressure.

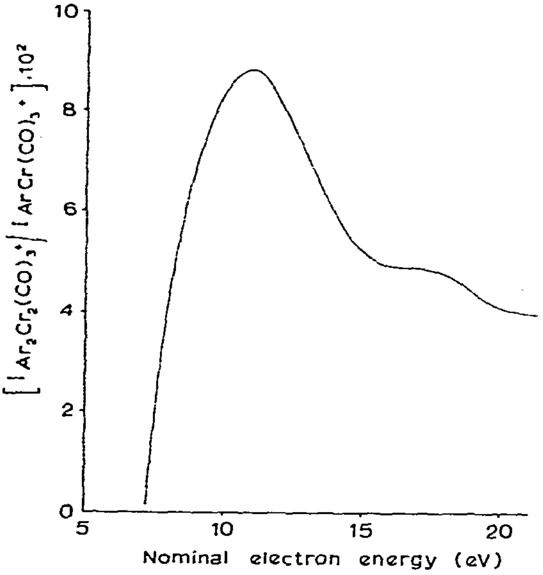


Fig. 2.

It can be seen that the secondary ion is enhanced relative to the parent ion at low electron energies and in fact there is a maximum in the curve showing some of the secondary ions to be formed in a resonance capture process. Such behaviour is typical of many ion-molecule reactions.

FRAGMENTATION PATHWAYS

It has become common practice when discussing the mass spectra of organometallic carbonyl compounds to refer to fragmentation of carbonyl groups as a "cascade loss". In some respects this terminology is both misleading and incorrect since loss of successive carbonyl groups from most organometallic compounds occurs rarely without competitive fragmentation of an alternative ligand[9]. In the spectra of these binuclear ions successive loss of carbonyl groups does occur and is confirmed by the existence and position of metastable peaks for almost all the compounds studied. Nonetheless there still exists competitive fragmentation in the loss of arene from the parent ion which in all cases becomes the energetically favoured process prior to the loss of the third carbonyl group. Further, the ion $[Ar_2Cr]^+$ also appears at low energies and may arise from a rearrangement of the parent binuclear ion. It is worth noting that a very similar rearrangement[10] occurs in the mass spectra of the cyclopentadienyliron dicarbonyl dimer to give the ferricinium ion $[(C_5H_5)_2Fe]^+$ at low energies[11].

We cannot however rule out the possibility of Ar_2Cr^+ being formed by an independent route such as the ion–molecule reaction, *viz.*:

$$ArCr(CO)_3 + [ArCr(CO)_3]^+ \rightarrow [Ar_2Cr]^+ + Cr(CO)_6$$

In the spectra of the trinuclear ions only fragment ions corresponding to losses of carbonyl are observed which is similar to the spectra of the mononuclear tricarbonyls where peaks corresponding to $[Cr(CO)_n]^+$ are also absent.

The appearance potentials of the binuclear cations are within experimental error the same as the ionisation potentials of the parent compounds and hence demonstrate the same substituent effect as their precursors[12,13]. No substituent effect is apparent in the appearance potentials of the fragment ions.

From a study of the positions of the metastable peaks and values of the appearance potentials of the ions measured we have formulated the general fragmentation pathway depicted in Scheme 1. It is to be expected that many more metastable peaks exist in the spectrum but since most of these would occur in the mass range of the mononuclear ion spectra they are obscured by intensity saturation.

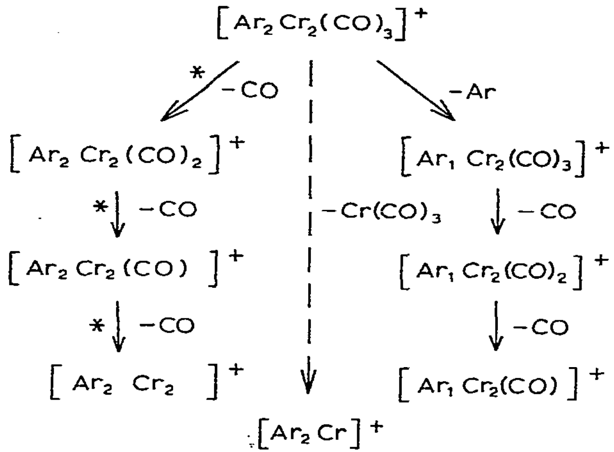
We have not been able to measure the appearance potential for the ions $[Ar_2Cr_2CO]^+$ owing to their low intensities.

As might be expected, identification and measurement of the spectra of the trinuclear species has been very much more difficult due to the very low intensities of these ions ($\approx 10^{-9}$ parent compound); however mass marking and isotope pattern measurements have shown the ion to be $[Ar_2Cr_3(CO)_6]^+$. The spectrum shows the loss of 1, 2, 3 and 4 carbonyl groups, the loss of the fifth and sixth being obscured by the binuclear ion spectra. Only one metastable peak is observed in the spectra of the trinuclear ions corresponding to the process:

$$[Ar_2Cr_3(CO)_6]^+ \xrightarrow{*} [Ar_2Cr_3(CO)_5]^+ + CO$$

SCHEME 1

FRAGMENTATION PATHWAY OF $[Ar_2Cr_2(CO)_3]^+$



As mentioned earlier there appears to be no competitive loss of arene during fragmentation of successive carbonyl groups, in contrast to the fragmentation of the binuclear ions.

The appearance potentials have been measured in the cases mentioned earlier and while the error must necessarily be high on such low intensity ions there seems little doubt that the formation reaction is between the binuclear ion and the parent molecule and that further increase in pressure would result in larger cluster ions which are unfortunately beyond the sensible detection limits of our present equipment.

EXPERIMENTAL

The mass spectra were measured with an A.E.I. MS 12 instrument with an ionising potential of 50 eV, trap currents of 100 and 20 μA and an ion accelerating voltage of 8 kV. The samples were introduced into the mass spectrometer by means of a direct insertion probe. Ion source pressures, measured on an A.E.I. V.C.9 ionisation gauge were between 5 and 8×10^{-6} mmHg for measurement of binuclear spectra and 8×10^{-6} to 2×10^{-5} mm Hg for the trinuclear spectra. The ion chamber temperature was maintained at 120° throughout.

Appearance potentials were determined using a semi-logarithmic method, employing helium, argon and krypton as standards and using a computer program operating over the linear range of the ionisation efficiency curve to calculate the potentials at the $\bar{2}$ level. We would consider an experimental error of ± 0.2 eV to be reasonable in measurement of binuclear ion appearance potentials.

Mass marking was carried out using tris(nonafluorobutyl)amine as a standard. The formulae for peaks at high masses were confirmed by comparison with calculated isotope abundance patterns.

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