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# THERMAL DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS IN THE ION SOURCE OF A MASS SPECTROMETER*

S. PIGNATARO** AND F. P. LOSSING
*Division of Pure Chemistry, National Research Council of Canada, Ottawa (Canada)*

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## INTRODUCTION

In the last few years a large number of new organometallic compounds have been synthesized and studies of their characteristics and structural properties are of current interest. A number of mass spectra[1-22] have been reported, and for some compounds the molecular ionization potentials[1-8] and appearance potentials of positive[1-7] and negative[3,20] fragment ions have been obtained. A comparison*** of the mass spectra and the appearance potentials reported, however, shows rather large discrepancies. The present study was carried out in an attempt to see if these discrepancies could result mainly from thermal decomposition effects in the mass spectrometer ion sources. The results reported here show that many organometallic compounds are extremely susceptible to such effects, and that in these cases analytical and energetic data can be seriously affected by spurious features in the mass spectra. This conclusion is in general agreement with that reported recently by Junk and Svec in a concurrent study of thermal decomposition effects in the mass spectrometry of related compounds[24].

## EXPERIMENTAL

The spectra were investigated using two 90° sector mass spectrometers with widely differing ion source temperatures. One of these, previously described[25], had an ambient source temperature of 250–300°, and was equipped with a low pressure capillary furnace through which the incoming sample passed just before entering the ionization chamber. Changes in furnace temperature cause no significant change in the cracking pattern of stable species, presumably since a large fraction of the molecules are in contact with the walls of the ion source before ionization. This instrument will be referred to as $S_1$. The second mass spectrometer, $S_2$, was a Perkin-Elmer-Hitachi RMU-6D, in which the ion source temperature was 60–70° with the auxiliary source heater turned off. When possible, samples were introduced by means of a sample-injection probe to avoid thermal decomposition effects in the sample reservoir.

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*** For a complete bibliography on these results see the review article on organometallic mass spectrometry by Bruce[23].

The appearance potential curves were evaluated by a "curve-matching" procedure[25]. The electron accelerating potentials in $S_1$ and $S_2$ were measured by means of a digital voltmeter isolated from ground potential. It is of interest to note that $S_2$ showed the same space-charge phenomena already noted with the Atlas $CH_4$[26] and CEC21-103[27] instruments. In order to get satisfactory ionization efficiency curves it was necessary to:

(*a*) reduce the total emission current to the lowest value at which it could be stabilized ($\sim$20 $\mu$ amp.)

(*b*) reduce to zero the voltages of the two repellers and the "grid" (filament shield), keeping the lens electrodes at the potentials required for maximum sensitivity.

(*c*) some improvement in space-charge interference was obtained by using the maximum ion accelerating potential (3600 V).

The linearity of the electron energy scale was checked occasionally by comparing measured ionization potentials for Kr, Xe, and 2-methyl-2-butene.

All the compounds studied were commercial samples, except for $Co(CO)_3NO$, which was a gift from Prof. A. Foffani.

## RESULTS AND DISCUSSION

The various decomposition effects observed are discussed below.

### *$Fe(CO)_5$*

This compound was found to decompose in the furnace of $S_1$ at a low temperature, giving mainly $Fe(CO)_4$ and CO. By 150° the extent of decomposition was 20–30%, as shown by a decrease in the parent peak and an increase in the *m/e* 28 peak. At the same time the $Fe(CO)_4^+$ peak increased by 20% with respect to the parent peak. A second phenomenon was a continual decrease in the height of all peaks, except the *m/e* 28 peak which continually increased. This occurred even with the furnace turned off. Under these conditions it was found that the simultaneous introduction of a small amount of air caused the following to occur:

(a) the parent ion intensity increased 8-fold;

(b) the ratio $Fe(CO)_4^+/Fe(CO)_5^+$ increased from 1.3 to 1.7;

(c) the pressure in the ion source decreased, indicating a reduction in the amount of decomposition.

The addition of traces of $CS_2$ instead of air caused a similar effect. On shutting off the stream of added air or $CS_2$ and setting the furnace temperature to 100°, the ratio $Fe(CO)_4^+/Fe(CO)_5^+$ decreased over one hour from 1.7 to 1.08 and became constant at that value. In $S_2$, with the source heater off, this ratio was also 1.08. Under these conditions the appearance potential of $Fe(CO)_4^+$ was 9.1$\pm$0.2 V in both instruments. Under the conditions in $S_1$ where the $Fe(CO)_4^+/Fe(CO)_5^+$ ratio was 1.7, the appearance potential of $Fe(CO)_4^+$ was reduced to 8.48 V (Table 1).

This unusual behavior can be explained as follows. The $Fe(CO)_5$ decomposes slowly at source temperatures of around 100° by loss of successive CO fragments. A film of Fe is deposited on the source plates, on which the rates of decomposition of $Fe(CO)_5$, and particularly those of the intermediate decomposition products $Fe(CO)_4$ etc., are catalytically enhanced. Under these conditions the ratio $Fe(CO)_4^+/Fe(CO)_5^+$ is approximately that of the parent substance, but the apparent sensitivity is greatly reduced, and a large amount of CO is formed. The addition of small amounts of oxygen or $CS_2$ poisons the catalytic Fe film, as shown by the reduction in the $CO^+$ peak and the increase in the parent peak. The increase in $Fe(CO)_4^+/Fe(CO)_5^+$ ratio, under conditions where $Fe(CO)_4$ is being produced by thermal decomposition in the furnace, shows that the poisoning is more effective for this species than for the parent compound. The decrease in appearance potential for $Fe(CO)_4^+$ accompanying the increase in $Fe(CO)_4^+/Fe(CO)_5^+$ ratio under these conditions of poisoning indicates that the lower value most probably corresponds to the ionization potential of free $Fe(CO)_4$, and that the higher value refers to the threshold for the dissociative ionization of $Fe(CO)_5$ to give $Fe(CO)_4^+$. It seems probable therefore that the appearance potential for $Fe(CO)_4^+$ measured[1] under conditions where the $Fe(CO)_4^+/Fe(CO)_5^+$ ratio was as high as 1.3, corresponds to $I[Fe(CO)_4]$ rather than to $A[Fe(CO)_4^+]$ from $Fe(CO)_5$. On this basis, and using the relationship

TABLE 1

APPEARANCE POTENTIAL CHANGES RESULTING FROM THERMAL DECOMPOSITION EFFECTS

| *Parent molecule* | *Ion* | *Ion source* 250–300° ($S_1$) | *Ion source* 60–70° ($S_2$) |
|---|---|---|---|
| $Fe(CO)_5$ | $Fe(CO)_4^+$ | 8.48 | 9.10 |
| $Co(CO)_3NO$ | $Co(CO)_2NO^+$ | 9.30 | 9.65 |
| $C_5H_5Co(CO)_2$ | $C_5H_5Co^+$ | 10.1 | 10.8 |

$$A[Fe(CO)_4^+] - I[Fe(CO_4)] \geqslant D[Fe(CO)_4–CO]$$

the present data give $D[Fe(CO)_4–CO]$ in $Fe(CO)_5$ as 0.7 ± 0.3 eV. The mean bond energy is 1.2 eV[28]. The relative weakness of the first bond presumably accounts for the ease of detection of the $Fe(CO)_4$ species in an ion source at temperatures above 100°.

### *$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$*

The decomposition of these compounds in the furnace of $S_1$ began at about 300°. Their stability shows that such compounds can be studied in a relatively hot ion source, and that earlier work[1,7,20-22] is not seriously affected by thermal decomposition effects. At furnace temperatures above 300° the ratio $M(CO)_5^+/M(CO)_6^+$ increased, indicating the formation of the $M(CO)_5$ species[29]. The maximum increase in ratio, less than 10%, was insufficient to permit measurements of their ionization potentials. A large increase of $CO^+$ intensity with furnace temperature above 300° confirmed that extensive decomposition was taking place.

### *$C_5H_5Co(CO)_2$*

This compound decomposed in the ion source of $S_1$, giving much larger *m/e* 66 and 65 peaks than were obtained using $S_2$, and than were reported in earlier work[3]. In addition, a peak at *m/e* 189 was found in $S_1$, identified from its mass and ionization potential as cobaltocene. Raising the furnace temperature in $S_1$ above 250° caused increased formation of *m/e* 189, 66 and 65. The *m/e* 189 peak showed a maximum at

350°. In $S_2$ no m/e 189 peak was observed, and $A(C_5H_5Co^+)$ was about 0.7 V higher than that measured in $S_1$. Evidently free $C_5H_5Co$ was produced in $S_1$ by pyrolysis in the hot ion source and also in the furnace. For such compounds it is clear that the use of a mass spectrometer with a hot ion source would give erroneous results not only for appearance potential measurements but for analytical results as well. This point is of particular importance in mass spectrometric measurements intended to establish the structural formulas and purity of new organometallic compounds[15-19]. Recent investigations in the laboratories of one of the authors (S.P.) have shown a similar effect for $Fe_2(CO)_9$ and for $M(CO)_5L$ (where M is Cr, Mo and W, and L is pyridine). Using a "hot" ion source and introducing samples through the gas inlet of an Atlas $CH_4$, the spectra of these compounds were found to be mainly those of $Fe(CO)_5$ and $M(CO)_6$ respectively. Combined phenomena of decomposition and recombination giving $Co_2(NO)_4BrCl$ from $Co_2(NO)_4Br_2 + Co_2(NO)_4Cl_2$ have also been observed in the inlet system of a MS9 (A.E.I.) instrument[10].

### $Co(CO)_3NO$

The ratio $Co(CO)_2NO^+/Co(CO)_3NO^+$ in $S_2$ at an ion source temperature of 60–70° was 0.98. In $S_1$ this ratio was 1.07. Under these conditions the appearance potential of $Co(CO)_2NO^+$ was 0.35 V lower in $S_1$ than in $S_2$ (Table 1). On raising the furnace temperature in $S_1$ to 150° the ratio increased to 1.25. These results show that the subcoordinated species $Co(CO)_2NO$ is formed by thermal decomposition in $S_1$ at an ion source temperature of 250–300°, and a further yield is obtained by thermal decomposition in the furnace. The yield was, however, too small to allow a reliable measurement of its ionization potential.

### $(C_6H_6)_2Cr$

This compound decomposed to a large extent in the ion source of $S_1$, and also in its inlet system, giving a metallic mirror. On increasing the sample pressure the parent peak increased, but decreased again almost immediately, suggesting a catalyzed decomposition with further deposition of a catalytic surface. On increasing the furnace temperature to 170°, an accelerated decomposition occurred. In $S_1$ the spectrum consisted mainly of m/e 78, corresponding to free benzene, with low abundance of all other fragments. The mass spectrum and ionization potential of $(C_6H_6)_2$-Cr obtained using $S_2$ have been reported[5] recently.

### $C_6H_6Cr(CO)_3$

Similarly to the behaviour of the Group VI metal carbonyls, this compound decomposed in the furnace of $S_1$ at about 300°. The main volatile products were benzene and CO. No formation of $(C_6H_6)_2Cr$ was observed. The mass spectrum and ionization potential of $C_6H_6Cr(CO)_3$ obtained using $S_2$ have been reported along with those of $(C_6H_6)_2Cr$[5].

### $Ni(CO)_4$

Using $S_1$ the only ion of any significant abundance was m/e 28, showing that the compound was completely decomposed to CO in the ion source. On the other hand a spectrum of $Ni(CO)_4$, resembling those of other metal carbonyls, has been obtained[4] using a Bendix time-of-flight mass spectrometer whose ion source is relatively cool* (~40°). By the use of a molecular beam inlet system, a spectrum free from pyrolytic interference has been obtained[30].

### $(C_5H_5)_2Fe$, $(C_5H_5)_2Co$, $(C_5H_5)_2Ni$, *acetylferrocene*

The present experiments indicate that these compounds can be studied using hot ion sources without any danger of decomposition. Using the furnace of $S_1$, the onset of decomposition for these compounds was at the following temperatures: 700–800° for $(C_5H_5)_2Ni$ and $(C_5H_5)_2Co$, 850–950° for acetylferrocene, and 900–1000° for $(C_5H_5)_2Fe$. For all these compounds the formation of $C_5H_5$ radical and of $C_5H_6$ (from abstraction of H on the reactor walls by $C_5H_5$) was observed. A slight increase in the ratio $(C_5H_5)M^+/(C_5H_5)_2M^+$ with furnace temperature was found suggesting the formation of the $C_5H_5M$ intermediates. On account of the low yield and the long tails on the appearance potential curves for the corresponding fragment ions from the parent compounds, no reliable ionization potentials for the fragments could be obtained. The coincidence of the onset for thermal decomposition of cobaltocene with that of nickelocene suggests that the dissociation energy of the $C_5H_5Co{-}C_5H_5$ bond is comparable to that in nickelocene (mean $\bar{D} = 56.6 \pm 10$ kcal/mole[28]) and lower than that in ferrocene (mean $\bar{D} = 69.5 \pm 10$ kcal/mole[28]).

## CONCLUSION

For studies on organometallic compounds the temperature of the ion source and of the introduction system are crucial factors. Most of the compounds discussed here were reasonably stable at an ion source temperature of 60–70°, but showed evidences of decomposition at temperatures of 250–300°. Appearance potentials and analytical measurements are therefore quite liable to be seriously in error in instruments having ion source temperatures much above 200°.

As a general rule, thermal decomposition is to be suspected whenever it is found that the ligand ions ($CO^+$, $NO^+$, $C_6H_6^+$, $C_5H_5^+$ etc.) have by far the largest peak intensity in the spectrum. In cases where the decomposition results from the deposition of catalytic metal films, the continuous introduction of a small partial pressure of air (or other catalyst poison) can reduce the decomposition markedly. The use of a direct introduction probe, where applicable, is greatly to be preferred to the use of a standard gas sample inlet system. By the use of an Inghram-type chopped molecular beam inlet pyrolytic effects can be reduced to nearly zero[31], since the contact of the sample gas with the ionization chamber is largely avoided. The necessary modifications are not easily made to a standard commercial mass spectrometer, however.

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* Even at an ion source temperature of 40° some compounds may decompose partially. The mass spectrum of $Mn(CO)_5H$ for example[12] shows a *m/e* 28 peak intensity at least 20 times higher than any other peak in the spectrum, suggesting the occurrence of considerable thermal decomposition.

## SUMMARY

Some thermal decomposition effects in mass spectral measurements on several organometallic compounds have been investigated: $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $(C_6H_6)_2Cr$, $(C_5H_5)_2Co$, $(C_5H_5)_2Ni$, $C_6H_6Cr(CO)_3$, $C_5H_5Co(CO)_2$, $Co(CO)_3NO$. Some of these compounds decompose extensively in an ion source at 250°, but are stable in an ion source at 60–70°. The unstable neutral species $Fe(CO)_4$, $Co(CO)_2NO$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$ and $C_5H_5Co$ have been detected among the decomposition products of the corresponding carbonyls. From the measured ionization potential of $Fe(CO)_4$, a value of $D[Fe(CO)_4{-}CO] = 0.7 \pm 0.3$ eV is obtained.

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