Journal of Organometallic Chemistry, 426 (1992) 361–367
Elsevier Sequoia S.A., Lausanne
JOM 22359

The thermal dissociation process of metal carbonyls on the heated Re surface: $Fe(CO)_5$ and $Mn_2(CO)_{10}$

Toshihiro Fujii, Kouichi Kakizaki and Hiromasa Ishii
National Institute for Environmental Studies, Tsukuba, Ibaraki 305 (Japan)

(Received March 1, 1991)

Abstract

Thermal dissociation processes of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ were investigated under conditions where gaseous molecules impinge on an incandescent rhenium surface, using the surface ionization (SI) technique in conjunction with mass spectrometric detection.

In the case of $Fe(CO)_5$ this process is dominated by thermal dissociation of the compound in a sequential manner, releasing carbonyl ligands, followed by ionization of the dissociated species. In the case of $Mn_2(CO)_{10}$, a metal–ligand cleavage reaction occurs in competition with the metal–metal cleavage process and produces bare metal atoms and dimetallic species.

Introduction

Transition metal carbonyls have some of the most special properties of all the organometallic compounds used for studies of electronic structure [1–3], thermal chemistry (bonding) [4] and photochemistry [5]. For example, the decacarbonyl dimetal complex of manganese [6–9] was among the first metal–metal bonded systems to be subjected to a detailed photochemical investigation. These molecules, in which two $Mn(CO)_5$ subunits are joined solely by a metal–metal single bond, provide ideal systems with which to examine the competition between metal–metal and metal–ligand bond reactivity in the chemistry of transition metal carbonyl complexes.

The high quantum yield for dissociation of $Mn_2(CO)_{10}$, also found in most other transition metal carbonyls, shortens the time spent in the excited state and consequently results in structureless electronic absorption spectra and immeasurably small quantum yields of emission.

Dissociation processes for such highly dissociative organometallic compounds in which multiple reaction paths are available have been explored in experiments based on multiphoton dissociation/multiphoton ionization (MPD/MPI) [10–15],

---

Correspondence to: Dr. T. Fujii, National Institute for Environmental Studies, Tsukuba, Ibaraki 305, Japan.

molecular beam reactions [16], photodissociation (flash photolysis) [5, 17–19], electron impact ionization [4] and on many other chemical methods [20]. The recently developed MPD/MPI method is particularly well suited for the study of many important aspects of metal carbonyl chemistry [13–15], because of its high sensitivity to a variety of fragments and its general selection rules. Such experiments are particularly informative as to processes in the gas phase. However, there has been a lack of methods suited to probing dissociation processes at the gas/solid interface. Thus, new approaches in this direction would be valuable.

Among recently developed techniques, surface ionization (SI) [21,22] occupies a special position and is particularly suited for the study of organometallic chemistry at the gas/solid interface. The SI method also offers a special advantage in that it allows mass spectrometric detection, leading to unambiguous identification of signal carriers.

Recent surface ionization organic mass spectrometry (SIOMS) experiments [23] on metallocenes indicate [24] that efficient thermal dissociation is followed by ionization of thermally dissociated neutral products [25–27]. Thus, it is highly likely that the study of metal carbonyls by SIOMS could yield important information since metal carbonyls may show high ionization efficiency and high yields for dissociation.

Another advantage of this technique is that dissociation and ionization are accomplished at the same site. Efficient thermal dissociation produces a variety of dissociated species on the surface over a broad range of surface temperatures. These species can be probed on the same surface and no problem of transport exists. In other words, thermal decomposition at the gas/solid interface could be studied nicely with the SI technique.

However, there is a drawback associated with using this technique, which is that SI cross-sections are intractable. Consequently, no meaningful information can be obtained from intensities, hence no quantitative data can be obtained relative to competition among reaction pathways.

This report discusses thermal dissociation studies performed on transition-metal carbonyls of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ at the gas/solid interface. Experimental data relevant to the primary dissociation process and the competition between metal–metal and metal–ligand bond breakage are also discussed. $Mn_2(CO)_{10}$ exemplifies transition metal complexes containing metal–metal bonds. This is the first report to illustrate the applicability of the SI technique to the thermal dissociation process.

Experimental

Experiments were carried out using a Finnigan 3300 gas chromatograph quadrupole mass spectrometer equipped with a combined SI and EI ion source. The experimental set-up was the same as that used in a previous study [27,28] on surface ionization organic mass spectrometry. Briefly, in the SI mode, a pure Re surface (a ribbon filament) was placed in the manufacturer's EI ion source. The metal carbonyls underwent thermal dissociation on the Re surface, followed by ionization of the resulting dissociated species. In the present study, the Re surface was kept in the temperature range 1300–1800 K: higher than in the conventional SIOMS study.

Table 1

Thermal dissociation/ionization spectral data of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ formed on a heated Re surface. (T_e = 1650 K and 1360 K for $Fe(CO)_5$ and $Mn_2(CO)_{10}$, respectively)

Compounds [a] (M(amu), IE (eV))	Ion species	Relative intensity	Remarks
Pentacarbonyl iron (196, 7.95)	56, Fe^+	100	IE(Fe) = 7.87 eV
	168, $Fe(CO)_4{}^+$	36	IE[$Fe(CO)_4$] = 6.33 eV
	140, $Fe(CO)_3{}^+$	33	IE[$Fe(CO)_3$] = 7.40 eV
	112, $Fe(CO)_2{}^+$	9	IE[$Fe(CO)_2$] = 7.27 eV
	196, $Fe(CO)_5{}^+$	1.8	
Decacarbonyl dimanganese (390, 8.42)	55, Mn^+	100	IE(Mn) = 7.44 eV
	110, $Mn_2{}^+$	1.2	

[a] IE values are taken from refs. 29 and 41.

The ultimate vacuum in the analyzer tube measured by the ion gauge (VG-1, Wakaida, Tokyo) after bakeout was typically in the range of 10^{-8} Torr. The Re surface was always flash-heated in the ultimate vacuum before use.

Samples were purchased from Ieda chemicals (Tsukuba, Japan). Admission of $Fe(CO)_5$ was regulated by a variable leak valve (Granville-Phillips, series 203) to maintain pressure around 2×10^{-5} Torr. $Mn_2(CO)_{10}$ was sublimed at 80°C in a heated glass tube located inside a column oven of GC. The sample flowed through the connector tube (15 cm) into the ionization chamber region of the mass spectrometer. The sample pressure was maintained, around 2×10^{-5} Torr. This was high enough to allow the detection of less prominent peaks.

EI mass spectra from both samples were recorded before other data were collected to check for impurities. Good general agreement was found between the EI mass spectra obtained and the spectrum as reported in the literature.

Results and discussion

Mass spectra

The mass spectrometric results for the ions from $Fe(CO)_5$ and $Mn_2(CO)_{10}$ are presented in Table 1. The spectral data are those obtained at the optimum surface temperature (T_e) which gives the maximum ion signal for each carbonyl compound. Relative abundance of positive ions represents the relative intensity (normalized to 100 units at the base ion peak). All measurable ions are listed. Table 1 also presents the molecular weights, the available ionization energy (IE) values of the dissociated (fragment) species [29] and assignments of the observed ions.

For both metal carbonyls, the most abundant ion observed was the bare metal atomic ion. However, relative yields of neutral thermal products cannot be quantitatively estimated from these signal intensities because of the unknown ionization cross sections for different fragments.

For $Fe(CO)_5$, ions of the type $Fe(CO)_x{}^+$ ($x = 2$–5) were observed, suggesting that thermal dissociation of this compound proceeds through the successive loss of a single carbonyl group. On the other hand, $Mn_2{}^+$ ion was observed at a low intensity level for $Mn_2(CO)_{10}$. No carbonylated species ($Mn(CO)_x{}^+$, $Mn_2(CO)_x{}^+$) were detectable.

We note that: (1) the absorption of thermal energy on the surface at temperatures higher than 1300 K provides sufficient energy to remove several CO ligands, and (2) the detection of the bare dimetal ions (Mn_2^+) shows that the metal–metal bonds can survive the absorption of sufficient energy to dissociate all ten of the carbonyl ligands from the parent molecule and subsequently form neutral fragments of Mn_2.

Intensities of all the ion signals, including Mn_2^+, were found to scale linearly with the sample pressure. This result eliminates the possibility that the dimetal species detected arose from binary reactions so that $Mn_2(CO)_{10}$ on the surface decomposes to give gaseous CO, leaving a Mn surface which yields Mn^+ and then Mn_2^+ ions.

Mass peaks corresponding to the elimination of radicals, such as H, CH_3, OH from molecule M, are often observed for many organic compounds under experimental set-ups similar to the present one. Observation of these peaks is already well-documented as dissociative surface ionization (DSI) in which the formation of the radical products, with a low IE via surface reaction, is followed by surface ionization [30].

$$M \rightarrow (M\text{–}X) + X \qquad X = H, CH_3, OH \tag{1}$$

$$(M\text{–}X) \rightarrow (M\text{–}X)^+ + e \tag{2}$$

In the consecutive mechanism above, $(M\text{–}X)^+$ ions are observed only for (M–X) having an appropriate (not too high) IE. The present result clearly indicates the occurrence of such a DSI process; the sequential dissociation in the initial step is followed by ionization of the resultant neutral species.

The absence of detectable $Fe(CO)^+$ can be rationalized in terms of the IE value of 8.39 eV of the Fe(CO) species [28] being larger than that of the $Fe(CO)_n$ species ($n = 2$–5).

Surface temperature dependence

Surface temperature (T) dependence was studied for all the peaks of ion currents (i), and the results are shown in Fig. 1. The characteristic form of the i vs. T curves was essentially the same for both compounds. However, the surface temperature threshold (T_t) for ion production was different. The difference may be explained partly by the bond energy. The available evidence suggests that the $OC\text{–}Mn_2(CO)_9$ bond is weaker, with a reliable value for the energy required for dissociation of the first carbonyl is approximately 36 kcal/mol [31] than the $OC\text{–}Fe(CO)_4$ bond (55.3 kcal/mol [32]). This is consistent with the present observation that T_t for $Mn_2(CO)_{10}$ is lower than that for $Fe(CO)_5$.

The initial increase of the ion intensity with the surface temperature may be interpreted partly by the rate law for the desorption process, which must involve an activation step. However, it remains unclear why the decrease of the ion intensity with T is observed after reaching the maximum temperature.

The variation in the fractional ion abundance, as a function of surface temperature, is considered. In the case of $Mn_2(CO)_{10}$, as T is increased the fractional abundances of Mn_2^+ ions increase slightly, pass through a maximum at 1380 K and then decrease.

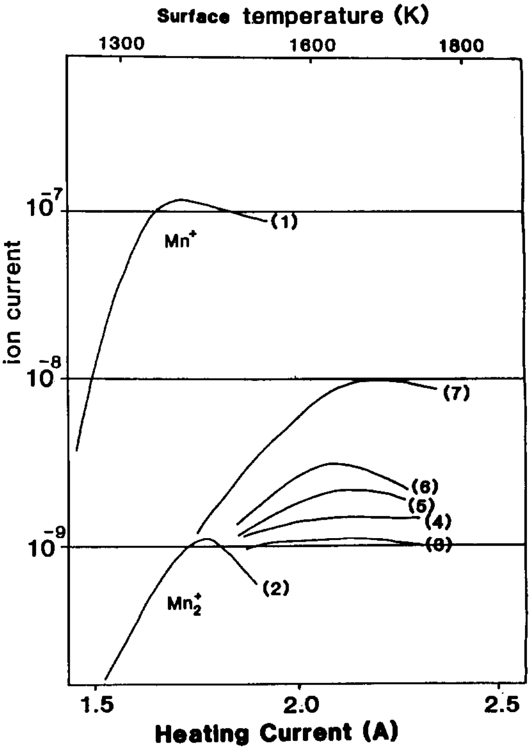

Fig. 1. Variation of resulting ion currents with surface temperature for $Fe(CO)_5$ and $Mn_2(CO)_{10}$. (1) Mn^+; (2) Mn_2^+; (3) $Fe(CO)_5^+$; (4) $Fe(CO)_2^+$; (5) $Fe(CO)_3^+$; (6) $Fe(CO)_4^+$; and (7) Fe^+.

Studies of the $Fe(CO)_5$ reveal it to behave differently. Ion current intensity ratios $Fe(CO)_x^+$ to Fe^+ remain almost constant over the examined temperature range.

Thermal dissociation pathway

Thermal dissociation/ionization of $Fe(CO)_5$ yields highly unsaturated metal-containing fragment ions in addition to atomic metal ions, suggesting that thermal dissociation proceeds through the successive loss of CO ligands.

On the other hand, the present results with $Mn_2(CO)_{10}$ indicate the occurrence of two competing processes [33–40]. The most likely dissociation processes for the formation of Mn^+ and Mn_2^+ are as follows:

$$Mn_2(CO)_{10} \rightarrow 2Mn(CO)_5 \rightarrow 2Mn + 10CO \qquad (3)$$

$$Mn_2(CO)_{10} \rightarrow Mn_2(CO)_x + (10-x)CO \rightarrow Mn_2 + 10CO \qquad (4)$$

This observation points to the interesting fact that, at the gas/solid boundary, thermal dissociation of $Mn_2(CO)_{10}$ proceeds by ligand dissociation both with and without the cleavage of the metal–metal bond. In other words, the dissociation reaction probably involves two or more intermediate dissociation pathways at the initial stage.

One pathway is the production of two $Mn(CO)_5$ units via clean, homolytic cleavage. Then, the $Mn(CO)_5$ radicals undergo successive loss of the ligands to metal atoms (reaction 3). The most likely assignment for the other pathway which eventually gives rise to the Mn_2^+ is the formation of partially decarbonylated complexes without metal–metal bond cleavage (reaction 4).

In addition, the Mn_2^+ signal intensity was found to vary linearly with the pressure of sample molecules, indicating that the dimetallic, ionic species are produced by direct dissociation, not as the result of any bimolecular reaction.

Conclusions

Mass analyses of ions produced on the heated Re surface for both metal carbonyls show that extensive dissociation occurs. Even near the surface temperature corresponding to the threshold for ion production, the M^+ metal ion is observed to be the dominant ion. The observation that M^+ always dominates over all other ions indicates that sequential dissociation dominates over desorption at all but the last stages of the ionization process.

Thermal dissociation of $Fe(CO)_5$ over a wide temperature range produces some partially decarbonylated products which retain the metal–CO bond.

The detection of Mn^+ and Mn_2^+ in the study of $Mn_2(CO)_{10}$ reveals that the process of thermal dissociation on a heated surface probably involves two or more intermediate dissociative pathways at the initial stage. Cleavage of the metal–metal bond might compete with that of the metal–CO bond.

A particularly interesting observation is the production of Mn_2^+ ions, which show that the metal–metal bonds can survive the absorption of sufficient energy to dissociate ten carbonyl ligands from the parent molecule.

In this study, the SI technique has been used directly to detect and characterize the dissociative products formed through the surface reaction for two models of metal carbonyl compounds. These species are representative of a broad class of dissociative products which are of general importance to organometallic material. Mass spectral data consist of qualitative information on the nature of the thermal dissociation process. This work illustrates the potential usefulness of the SI technique, coupled with mass spectrometry, to investigations of heterogeneous dissociation reactions.

References

1 R. Hoffmann, Science, 211 (1981) 995.
2 R.A. Levensen, H.B. Gray and G.P. Ceasar, J. Am. Chem. Soc., 92 (1970) 3653.
3 R.A. Levensen and H.B. Gray, J. Am. Chem. Soc., 97 (1975) 6042.
4 J.A. Conner, Top. Curr. Chem., (1977) 71.
5 T.J. Meyer and J.V. Caspar, Chem. Rev., 85 (1985) 187.
6 M.S. Wrighton and D.S. Ginley, J. Am. Chem. Soc., 98 (1975) 2065.
7 R.W. Wegman, R.J. Olsen, L.R. Faulkner and T.L. Brown, J. Am. Chem. Soc., 103 (1981) 6089.
8 D.A. Lichtin, R.B. Bernstein and V. Vaida, J. Am. Chem. Soc., 104 (1982) 1830.
9 R.S. Herrick and T.L. Brown, Inorg. Chem., 23 (1984) 4550.
10 L.J. Rothberg, D.P. Gerrity and V. Vaida, J. Am. Chem. Soc., 74 (1981) 2218.
11 G.J. Fisanick, A. Gedanken, T.S. Eichelberger, N.A. Kuebler and M.B. Robin, J. Chem. Phys., 75 (1981) 5215.
12 W.E. Hollingsworth and V. Vaida, J. Phys. Chem., 90 (1986) 1235.

13 A. Gedanken, M.B. Robin and N.A. Kuebler, J. Phys. Chem., 86 (1982) 4096.
14 H.W. Thompson and A.P. Garratt, J. Chem. Soc., (1934) 524.
15 M.A. Duncan, T.G. Dietz and R.E. Smalley, Chem. Phys., 44 (1979) 415.
16 G.W. Tyndall and R.L. Jackson, J. Chem. Phys., 91 (1989) 2881.
17 E.K.C. Lee, Acc. Chem. Res., 10 (1977) 319.
18 R.J. Olsen and T.L. Brown, Inorg. Chem., 23 (1984) 3784.
19 T. Kobayashi, K. Yasufuku, J. Imai, H. Yesaka, H. Noda and H. Ohtani, Coord. Chem. Rev., 64 (1985) 1.
20 R.E. Tecklenburg, Jr. and D.H. Rusell, J. Am. Chem. Soc., 109 (1987) 7654.
21 E.Ya. Zandberg and U.Kh. Rasulev, Russ. Chem. Rev., 51 (1982) 819.
22 T. Fujii and H. Arimoto, Am. Lab., (1986) August, 54.
23 T. Fujii, Int. J. Mass Spectrom. Ion Proc., 57 (1981) 63.
24 T. Fujii and H. Ishii, Chem. Phys. Lett., 163 (1989) 69.
25 N. Aristov and P.B. Armentrout, J. Am. Chem. Soc., 108 (1986) 108.
26 P.B. Armentrout, P.B. Hodges and J.L. Beauchamp, J. Chem. Phys., 66 (1977) 4683.
27 P.B. Armentrout and J.L. Beauchamp, J. Am. Chem. Soc., 103 (1981) 784.
28 T. Fujii, J. Phys. Chem., 88 (1984) 5228.
29 R.L. Whetten, K.J. Fu and E.R. Grant, J. Chem. Phys., 79 (1983) 4899.
30 T. Fujii, H. Suzuki and M. Obuchi, J. Phys. Chem., 89 (1985) 4687.
31 P.C. Engelking and W.C. Lineberger, J. Am. Chem. Soc., 101 (1979) 5569.
32 H. Wawersik and F. Basolo, Inorg. Chim. Acta, 3 (1969) 113.
33 A. Freedman and R. Bersohn, J. Am. Chem. Soc., 100 (1978) 4116.
34 N.J. Coville, A.M. Stolzenberg and E.L. Muetterties, J. Am. Chem. Soc., 105 (1983) 2499.
35 D.G. Leopold and V. Vaida, J. Am. Chem. Soc., 106 (1984) 3720.
36 T.A. Seder, S.P. Church and E. Weitz, J. Am. Chem. Soc., 108 (1986) 7518.
37 D.A. Pinslow and V. Vaida, J. Am. Chem. Soc., 109 (1987) 5097.
38 A. Fox and A. Poe, J. Am. Chem. Soc., 102 (1980) 2497.
39 S.P. Church, H. Hermann, F. Grevels and K.J. Schaffner, J. Chem. Soc. Chem. Commun., (1984) 785.
40 H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, J. Am. Chem. Soc., 105 (1983) 6249.
41 S.H. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin and W.G. Mollard, J. Phys. Chem. Ref. Data, (Suppl. No. 1), 17 (1988) 861 p.