Evolved gas analysis–ion attachment mass spectrometric analysis of decacarbonyl dimanganese pyrolysis

Yuki Kitahara · Toshihiro Fujii

Abstract Evolved gas analysis–ion attachment mass spectrometric analysis of the principal species produced by the pyrolysis of $Mn_2(CO)_{10}$ in an infrared image furnace indicated the presence of $Mn(CO)_5$ in the gas phase. This observation indicates that $Mn_2(CO)_{10}$ was in equilibrium with $Mn(CO)_5$. We also studied the temperature dependence of the mass spectrum to obtain information about the kinetics of the $Mn_2(CO)_5$ dissociation reaction. From the temperature dependence of the peak for $Mn(CO)_5Li^+$ (m/z 202), we calculated the apparent activation energy of $Mn(CO)_5$ dissociation from solid $Mn_2(CO)_{10}$. The calculated activation energy (274.57 kJ/mol) is compared with previously reported experimental and calculated values of Mn–Mn bond dissociation energies.

Keywords Evolved gas analysis · Ion attachment mass spectrometry · Decacarbonyl dimanganese · Pyrolysis · Apparent activation energy

Introduction

Transition metal carbonyls are used for the commercial synthesis of CO compounds and have potential for use as heterogeneous catalysts [1, 2] in organometallic chemistry. Information about the metal–metal bond energies, $D(M-M)$, in metal carbonyl clusters can be expected to improve our understanding of reaction kinetics, product composition and yields of reaction systems. Over the past decades, large quantities of experimental data have appeared for the $D(Mn-Mn)$ bond energies of $Mn_2(CO)_{10}$ [3–13].

Using information gained in our previous studies of Li^+ ion attachment mass spectrometry (IAMS) [14–17], we recently showed that during evolved gas analysis (EGA)–IAMS studies of the pyrolysis of $Mn_2(CO)_{10}$ in an infrared image furnace (IIF), $Mn(CO)_5$ is present in the gas phase [18], providing direct evidence that d–metal complex radicals are formed in the IIF. The temperature dependence of the spectrum has also be evaluated with a view toward increasing the rate of product formation and confirming that $Mn_2(CO)_{10}$ undergoes the following dissociation reaction:
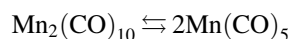
$$Mn_2(CO)_{10} \leftrightarrows 2Mn(CO)_5$$

We report here our EGA-IAMS investigation of the thermal pyrolysis of $Mn_2(CO)_{10}$ and our calculation of the apparent activation energy (E_a) for dissociation of $Mn(CO)_5$ from solid $Mn_2(CO)_{10}$. Unlike traditional mass spectrometry (which involves ionization by high-energy electrons), EGA-IAMS offers a considerable advantage in that it preserves the structure of $Mn(CO)_5$ molecules, allowing their detection as unfragmented adduct ions.

Experimental

Apparatus

We used a homemade system consisting of an atmospheric-pressure IIF coupled to a Li^+ IAMS (Canon Anelva, Kawasaki, Japan) (Fig. 1). The construction of the IIF inlet system has been reported in detail elsewhere [15]. The

Y. Kitahara · T. Fujii (✉)
Department of Chemistry, Faculty of Sciences and Engineering, Meisei University, Hodokubo 2-1-1, Hino, Tokyo 191-8506, Japan
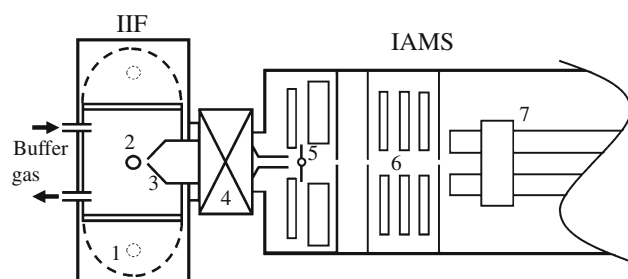e-mail: fujii@chem.meisei-u.ac.jp

Fig. 1 Schematic diagram of the evolved gas analysis–ion attachment mass spectrometry system used for thermal analysis of solid $Mn_2(CO)_{10}$ in a nitrogen flow at 105 Pa. *1* IR lamp unit, *2* sample holder, *3* 70 μm orifice, *4* gate valve, *5* Li$^+$ ion emitter bead fused onto an Ir wire, *6* focus lens, *7* quadrupole mass spectrometer

IFF (RHL-E45P, Sinku-Riko Corp., Tokyo, Japan) was employed as the heat source. A $Mn_2(CO)_{10}$ sample in a quartz pan was subjected to temperature-programmed heating in the IFF. The dissociation products were swept by a nitrogen stream, at a flow rate in the 250–300 mL/min range and a pressure of 1 atom, through an orifice into the mass spectrometer.

The IIF was also used as a temperature-programmed flow reactor for kinetic studies of $Mn_2(CO)_{10}$ dissociation by means of a previously described procedure [18]. The heating rate of 20 °C/min was chosen to avoid heat transfer limitations. This choice was based on the report [19] that boundary for particle size was constructed as a function of the temperature, by comparing characteristic times for reaction rates versus heating rates. We used the Arrhenius equation to calculate E_a for dissociation of $Mn(CO)_5$ using mass spectrometry data obtained in selected ion monitoring mode.

Samples

Powdered $Mn_2(CO)_{10}$ (sample amount, 1 mg; particle diameter, 50 μm; 99% purity) was purchased from Aldrich (Tokyo, Japan) and used as received. No impurities were detected by mass spectrometry. The nitrogen buffer gas was purified by passage through a drying tube containing 5 Å molecular sieves.

Results and discussion

Mass spectra

$Mn_2(CO)_{10}$ was subjected to temperature-programmed heating at a rate of 20 °C/min in the IIF. The total ion monitoring curves for $Mn_2(CO)_{10}$ showed (Fig. 2, inset) only one maximum located below 170 °C. The ion attachment mass spectra of the products obtained from

pyrolysis of $Mn_2(CO)_{10}$ at furnace temperatures of 95 and 145 °C (Fig. 2) under nitrogen showed peaks corresponding directly to the thermal dissociation products, because IAMS provides only molecular ions for each product species. The mass spectrum at 95 °C (Fig. 2, upper panel) showed a peak at m/z 202, which we assigned as $Mn(CO)_5$ radical species. The presence of neutral products was indicated by an increase in the current of the Li$^+$ adduct ions.

The appearance of many peaks as products of $Mn_2(CO)_{10}$ pyrolysis was initiated by the thermal energy. The spectrum at 145 °C (Fig. 2, lower panel) clearly showed an intense peak at m/z 202 for $Mn(CO)_5Li^+$, together with small peaks at m/z 63, 203, 229, 257, and 369, suggesting that $(CO)_2Li^+$, $HMn(CO)_5Li^+$, $Mn_2(CO)_4Li^+$, $Mn_2(CO)_5Li^+$, and $Mn_2(CO)_9Li^+$, respectively, were formed in the gas phase.

An important objective of this study was to determine the fraction of $Mn_2(CO)_{10}$ degraded to the reactive byproduct $Mn(CO)_5$ during the programmed heating. The reaction equilibrium was investigated by comparison of data obtained during variation of the furnace temperature.

Apparent activation energy for dissociation of $Mn(CO)_5$ from $Mn_2(CO)_{10}$ in the solid state

A pyrogram (also referred to as a thermogram) obtained in selected ion monitoring mode from an EGA system can provide information about the relative proportions of the observed molecules, which in turn indicates their relative production rates. In this study, we used EGA-IAMS to evaluate the temperature dependence of the peak for $Mn(CO)_5Li^+$ (m/z 202) to obtain information about the dissociation of $Mn(CO)_5$ from $Mn_2(CO)_{10}$. The inset of Fig. 3 shows a pyrogram, obtained in selected ion monitoring mode ($Mn(CO)_5Li^+$, m/z 202), of $Mn_2(CO)_{10}$ subjected to temperature-programmed heating to 500 °C in the IFF. The presence of a clear peak suggests that $Mn(CO)_5$ was released in free radical form.

Dissociation of chemical compounds may involve a complicated set of competing reactions. In this study, we assumed that

$$d\alpha/dt = kx(1 - \alpha) \tag{1}$$

where α is the degree of yield of the decomposition product and k is the rate constant of the decomposition reaction; we also assumed that the reaction was first order (that is, we assumed a unimolecular dissociation reaction). The temperature dependence of the rate constant may be approximated by a simple Arrhenius equation: $k = Ae^{-(E_a/RT)}$, where A is the frequency factor, and E_a is the apparent activation energy. Equation 1 can be transformed into

Fig. 2 Ion attachment mass spectra of products obtained from $Mn_2(CO)_{10}$ at furnace temperatures of 95 °C (*upper panel*) and 145 °C (*lower panel*) under nitrogen. Samples were placed in the furnace and then heated from room temperature to 800 °C at a linearly programmed rate of 20 °C/min
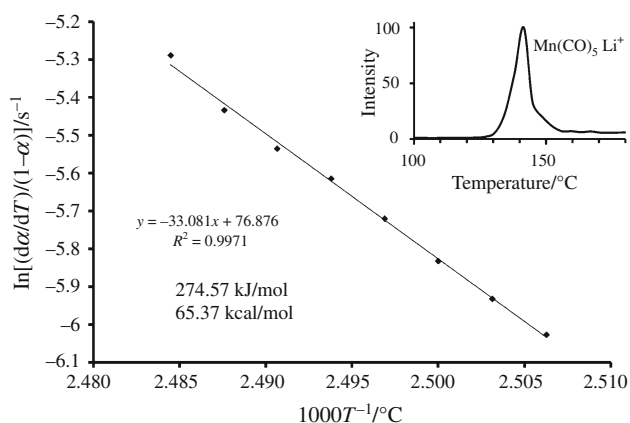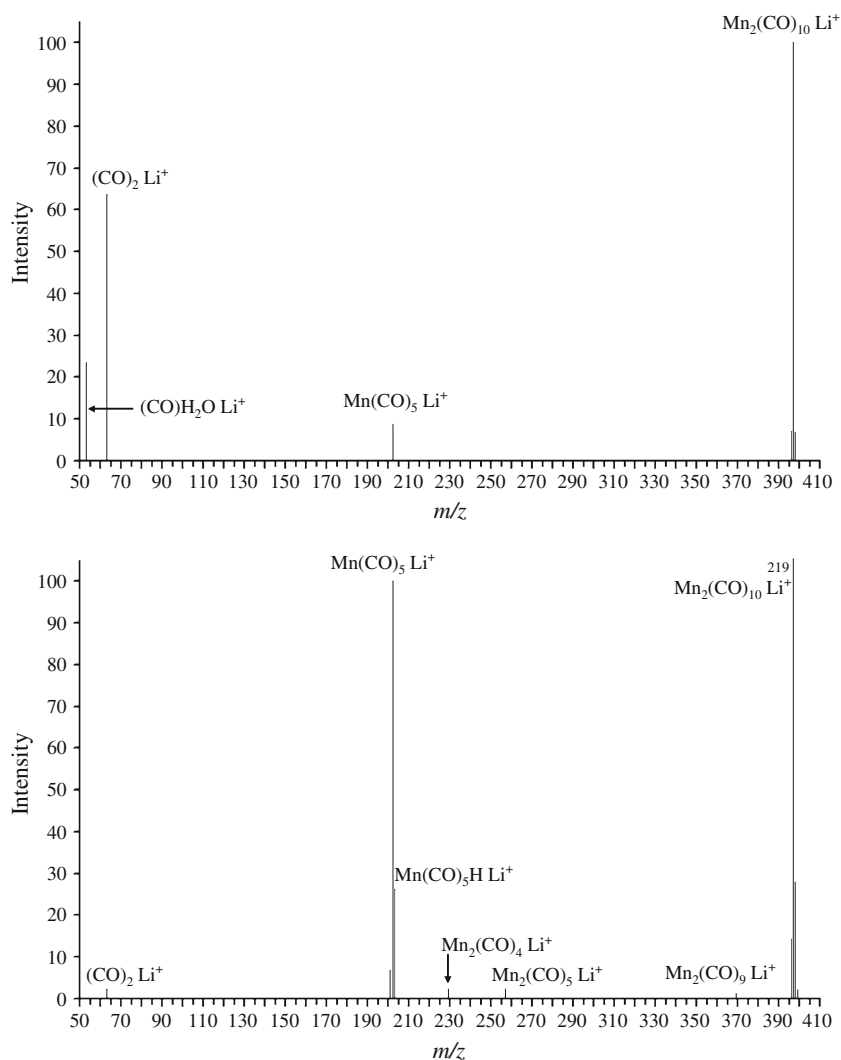
Fig. 3 Arrhenius plot of $Mn(CO)_5Li^+$ signal intensity versus $1/T$ in the temperature range from 125 to 130 °C. *Inset*: evolved gas analysis curve for $Mn(CO)_5$ obtained in selected ion monitoring mode from the relative ion intensities for $Mn(CO)_5Li^+$ (m/z 202) during temperature-programmed heating in the infrared image furnace

$$d\alpha/dT = Ae^{-(E_a/RT)}(1 - \alpha) \tag{2}$$

Mathematically, this equation cannot be easily solved. To overcome this difficulty, we used the Knumann [20] approximation, which applies multiple linear regressions to the logarithmic form of Eq. 3:

$$\ln(d\alpha/dT) = \ln(A) - E_a/RT + \ln(1 - \alpha) \tag{3}$$

The ion signal intensity (i) acquired by real-time selected ion monitoring of $Mn(CO)_5Li^+$ (Fig. 3) produced during pyrolysis of $Mn_2(CO)_{10}$ was used to obtain the functional form of the kinetic rate expression. From plots of $\ln i$ versus $1/T$, E_a could be determined [15, 16]. We investigated i for the $Mn(CO)_5Li^+$ signal at m/z 202 over the temperature range 125–130 °C to obtain the rate expression for $Mn(CO)_5$ dissociation; we assumed that there was a simple correlation between the adduct ion signal intensity and the product concentrations and that the reaction exhibited first-order

Table 1 Theoretically predicted and experimentally observed bond dissociation energies and activation enthalpies for bond homolysis for $Mn_2(CO)_{10}$, ΔH/kJ/mol

D(Mn–Mn)	ΔH for Mn–Mn bond homolysis	Method	Reference
143 ± 55		Thermochemical estimate	[4]
	153.8	Photolysis	[12]
94 ± 13		Mass spectrometry	[7]
88 ± 14		Van't Hoff	[7]
104 ± 13		Mass spectrometry	[8]
	153.8 ± 1.6	Thermochemical estimate	[5]
	94	Thermochemical estimate	[6]
155		Thermochemical estimate	[11]
171		Photoelectron spectroscopy	[9]
159 ± 21		Photoacoustics calorimetry	[10]
173		Density functional theory	[13]
135		Density functional theory	[21]
163		Density functional theory	[22]

kinetics. The slope of the plot of signal intensity versus $1/T$ was constant (Fig. 3), and an E_a of 274.57 kJ/mol and an A of 2.44×10^{33} s^{-1} were calculated from the plot. At this time, we have no explanation for the large magnitude of A.

Concluding remarks

When it is assumed that the formation of $Mn(CO)_5$ is due mostly to sublimation and the subsequent breaking of the Mn–Mn bond of $Mn_2(CO)_{10}$, the E_a value likely reflects the energy of the Mn–Mn bond and the enthalpy of sublimation. In Table 1, we list all the experimentally observed and theoretically predicted bond dissociation energies and activation enthalpies for homolysis of the Mn–Mn of $Mn_2(CO)_{10}$. Experimental measurements of the Mn–Mn bond energy vary widely, from 88 to 171 kJ/mol, with the most recent measurements converging on a value of approximately 160 kJ/mol. The calculated Mn–Mn bond dissociation energies (173, 135, and 163 kJ/mol [13, 21, 22]) are in reasonable agreement with this value. The most recently reported value for the molar enthalpy of $Mn_2(CO)_{10}$ sublimation, obtained by means of a combustion calorimetry (static bomb) method, is 92.3 kJ/mol [23]. The E_a we determined is close to the sum of the enthalpy of

sublimation (92.3 kJ/mol) and the approximate bond dissociation energy (160 kJ/mol) of $Mn_2(CO)_{10}$.

In summary, we used an EGA-IAMS system with an IFF to determine E_a for the formation of $Mn(CO)_5$. To the best of our knowledge, no such experiment has previously been reported. We believe that this system will aid investigations of the mechanisms and kinetics of gaseous free radical reactions of other transition metal complexes.

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