Gas Phase Brønsted Basicity of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3]$

By JOSÉ FERNANDO, G. FAIGLE, ANA MARIA DA COSTA FERREIRA, SERGIO E. GALEMBECK, and JOSÉ M. RIVEROS*
(*Instituto de Química, Universidade de São Paulo, Caixa Postal* 20780, *São Paulo, Brasil*)

Summary The gas phase Brønsted basicity of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3]$ has been determined at 296 K by ion cyclotron resonance equilibrium measurements; these experiments enable us to calculate the proton affinity of this complex as being 825 ± 8 kJ mol^{-1} by using NH_3 as a reference.

THE recent determination of gas phase basicities and acidities from ionic equilibria measurements is a major breakthrough for solution chemistry.[1,2] While basicity scales have been established for a variety of organic functional groups and the simplest inorganic hydrides,[3,4] little is known about the proton binding ability of transition metal complexes in the gas phase. We report the quantitative determination of the gas phase Brønsted basicity of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3]$ by ion cyclotron resonance (i.c.r) spectroscopy.

The low pressure (7×10^{-5} N m^{-2}) i.c.r. spectrum of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3]$, obtained at room temperature and at 40 eV, is similar to the mass spectrum previously reported for the cyclopentadienyl complex.[5] At higher pressures, no new ions that could be ascribed as products of ion–molecule reactions of the complex could be detected in the 1—250 a.m.u. mass range. However, the i.c.r. spectra of mixtures of the complex and organic and inorganic bases reveal some important features: (a) the fragment ions and the protonated species of alcohols, aldehydes, water, ketones, phosphine, and the lower esters are observed to transfer readily a proton to the complex to yield the ion $[(\text{MeC}_5\text{H}_4)\text{Mn(CO)}_3\text{H}]^+$; (b) this process is not observed with ammonia, amines, and pyridine; and (c) several of the aforementioned bases (B) undergo ion–molecule reactions with fragment ions of the complex (Scheme).

$$[(\text{MeC}_5\text{H}_4)\text{Mn(CO)}]^+ + \text{B} \longrightarrow [(\text{MeC}_5\text{H}_4)\text{MnB}]^+ + \text{CO}$$

and

$$[(\text{MeC}_5\text{H}_4)\text{Mn}]^+ + \text{B} \longrightarrow [(\text{MeC}_5\text{H}_4)\text{MnB}]^+$$

SCHEME

The first two observations bracket the gas phase Brønsted basicity of the complex in the vicinity of that for several compounds for which accurate quantitative values are available.[4,6] A trapped ion pulsed i.c.r. system[6] was used to measure equilibrium constants of the acid–base process in the gas phase involving the protonated ions. A typical experiment consisted of ion formation pulses of 10 ms at total pressures not exceeding $1{\cdot}3 \times 10^{-4}$ N m^{-2}. The concentration of the protonated ions was followed up to 1 s after the formation pulse. The most thoroughly studied system reveals the equilibrium (1) in the gas phase. At the

$$\begin{aligned} &\mathrm{MeCO_2Et} + [(\mathrm{MeC_5H_4})\mathrm{Mn(CO)_3H}]^+ \\ &\rightleftharpoons [(\mathrm{MeCO_2Et})\mathrm{H}]^+ + [(\mathrm{MeC_5H_4})\mathrm{Mn(CO)_3}] \quad (1) \\ &(\Delta G^0_{296} = -\,2{\cdot}3 \pm 1{\cdot}0 \text{ kJ mol}^{-1}) \end{aligned}$$

pressures used for these measurements, no proton-bound dimers can be detected for esters or ketones. Thus, it is unlikely that similar species of the complex will be formed and interfere with the above equilibria. These experiments, coupled with the values recently determined for ethyl acetate,[3,4,6] allow us to place the manganese complex $16{\cdot}5 \pm 1{\cdot}0$ kJ mol^{-1} below NH_3 in the basicity scale. The proton affinity (p.a.) of $[(\eta^5\text{-}\mathrm{MeC_5H_4})\mathrm{Mn(CO)_3}]$ can then be calculated as being 825 ± 8 kJ mol^{-1} by correction of the entropy effects[3] and by using NH_3 as an absolute reference (p.a. of $NH_3 = 845 \pm 8$ kJ mol^{-1}).[4] The only other available data on transition metal complexes estimate the proton affinity of $[\mathrm{Fe(CO)_5}]$ to be *ca.* $12{\cdot}5$ kJ mol^{-1} below NH_3,[7] and of $[\mathrm{Fe(C_5H_5)_2}]$ to be *ca.* 25 kJ mol^{-1} above NH_3.[8]

Finally, it should be mentioned that trapped ion and double resonance i.c.r. experiments were carried out in ternary mixtures of the manganese complex and two different bases in order to test the relative stability of the $[(\mathrm{MeC_5H_4})\mathrm{MnB}]^+$ species (see Scheme), and thus the ligand ability of B. While quantitative data could not be obtained on these systems because of poor signal to noise ratio, ligand stability was observed to follow the order MeCN > MeCOEt > Me_2CO.

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