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DETERMINATION OF METAL–HYDROGEN BOND DISSOCIATION ENERGIES BY THE DEPROTONATION OF TRANSITION METAL HYDRIDE IONS: APPLICATION TO MnH^+

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ICR trapped ion techniques are used to examine the kinetics of proton transfer from MnH^+ (formed as a fragment ion from $HMn(CO)_5$ by electron impact) to bases of varying strength. Deprotonation is rapid with bases whose proton affinity exceeds 196 ± 3 kcal mol^{-1}. This value for PA (Mn) yields the homolytic bond dissociation energy $D^0(Mn^+–H) = 53 \pm 5$ kcal mol^{-1}.

1. Introduction

Transition metal hydrides are of considerable theoretical interest since they are the simplest species which can be studied to better understand the nature and energetics of sigma bonding in transition metal compounds [1–3]. Experimental interest in these species results, for example, from their observation in spectra of stellar atmospheres [3,4], their importance as reactive intermediates in homogeneous and heterogeneous catalysis [5], their use in hydrogen storage systems [6], and their involvement in schemes for interconversion of H_2, O_2 and H_2O [7]. Despite this, very little information is available concerning metal–hydrogen bond strengths. Several new approaches to this problem have been explored in our laboratories [8–10].

In the present work we demonstrate that studies of the kinetics of deprotonation of diatomic transition metal hydride ions,

$$MH^+ + B \rightarrow BH^+ + M\,, \qquad (1)$$

in which M = metal and B is a neutral n-donor base, can be used to quantify the base strengths (proton affinities) of metal atoms and provide metal–hydrogen homolytic bond dissociation energies, $D^0(M^+–H)$. The energetics of B and BH^+ are well characterized for a wide range of n-donor bases [11,12]. An examination of process (1) thus links the heats of formation of M and MH^+. Other examples where this experimental methodology has been successfully applied include determination of the heats of formation of CF_2 [13] and $(CH_3)_2SiCH_2$ [14] by examining deprotonation reactions of the corresponding conjugate acids.

2. Experimental

The experimental techniques and instrumentation for ion cyclotron resonance spectroscopy (ICR) have been described in detail [15]. All experiments were performed at ambient temperature (≈25°C in the ICR cell). Pressures were measured using a Schulz–Phelps gauge calibrated at higher pressures against a model 90H1-MKS Instrument capacitance manometer. Estimated accuracy of pressure measurements is ±20%, which determines the accuracy of rate constants.

$HMn(CO)_5$ was prepared as described in the literature and purified by degassing the sample held at −78°C until no impurities were detected in the mass spectrum [16]. This species slowly decomposes to yield trace amounts of H_2, CO, CO_2, and $Mn_2(CO)_{10}$, which do not interfere with the present experiments. Formalde-

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hyde was prepared by thermal cracking of the trimer and purified by vacuum distillation. All other samples were obtained from commercial sources and used as supplied except for degassing at liquid nitrogen temperature.

3. Results and discussion

Manganese hydride ion is observed as a fragment in the mass spectrum of $HMn(CO)_5$, comprising 10% of the total ion abundance at 70 eV. This species reacts with the parent neutral ($k = 1.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) as indicated in the equation

$$MnH^+ + HMn(CO)_5 \rightarrow Mn_2(CO)_4^+ + CO + H_2 . \qquad (2)$$

In the presence of a sufficiently strong n-donor base the disappearance of MnH^+ is more rapid. This is shown for the case of isopropyl cyanide in fig. 1. By taking the logarithm of the ratio of the MnH^+ signal intensity with and without added base (fig. 2), the rate of the proton transfer reaction

$$MnH^+ + (CH_3)_2CHCN \rightarrow (CH_3)_2CHCNH^+ + Mn \qquad (3)$$

is determined to be 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}. Continuous ejection of MnH^+ leads to a decrease in the abundance of $(CH_3)_2CHCNH^+$ which quantitatively accounts for the removal of MnH^+ and confirms the proton transfer process.

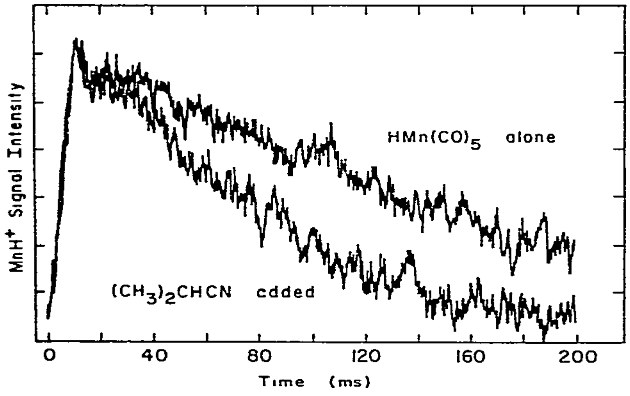

Fig. 1. Variation of the abundance of MnH^+ with time, following a 70 eV, 10 ms electron pulse. The upper curve depicts the decay of MnH^+ in the presence of 1.5×10^{-7} Torr $HMn(CO)_5$. The lower curve illustrates the increased rate of decay when 1.7×10^{-7} Torr of $(CH_3)_2CHCN$ is added.

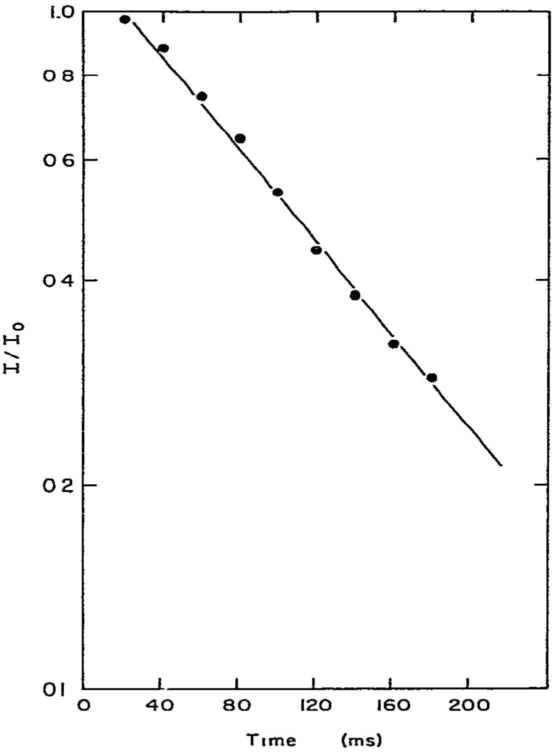

Fig 2 Ratio of the MnH^+ signal with and without added $(CH_3)_2CHCN$ as a function of time. Conditions are as in fig. 1.

Measured proton transfer rates are summarized in table 1, and compared to the calculated collision rates using the ADO analysis of Bowers and co-workers [17].

Table 1
Rate constants for reaction of proton acceptors with MnH^+

Proton acceptor B	$10^9 k$[a] (cm^3 molecule^{-1} s^{-1})	k/k_{ADO}[b]	PA(B)[c] (kcal mol^{-1}
NH_3	1.3	0.74	207.0
$(CH_3CH_2)_2O$	1.1	0.75	202.1
$(CH_3)_2CO$	1.1	0.50	198.6
$(CH_3)_2CHCN$	1.5	0.58	196.9
$(CH_3)_2O$	0.31	0.21	194.8
CH_3CN	no reaction	0.0	191.7
CH_3CHO	no reaction	0.0	189.1
CH_3OH	no reaction	0.0	186.9
CH_2O	no reaction	0.0	179.3

[a] The limit of detection is $k = 10^{-11}$ cm^3 molecule^{-1} s^{-1}.
[b] Calculated from the formula given in ref. [17].
[c] From refs. [11,12].

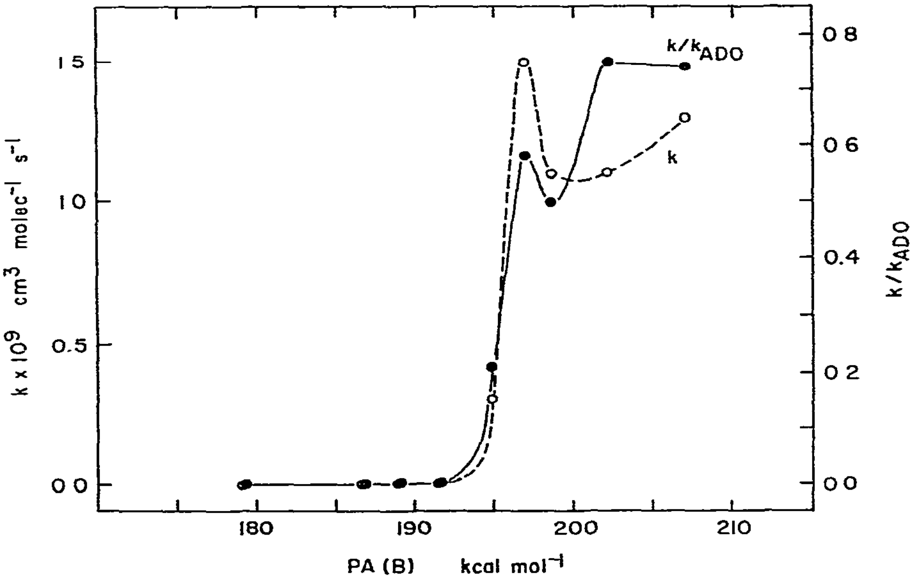

Fig. 3. Rate constants as a function of proton affinity of B for the reaction $MnH^+ + B \rightarrow BH^+ + Mn$. The open circles are the measured rate constants. Closed circles are the measured rate constants divided by the encounter rate, k/k_{ADO}.

These quantities are illustrated graphically in fig. 3 as a function of the proton affinity of the organic base. All proton affinity data are relative to $PA(NH_3) = 207.0$ kcal mol^{-1}. This value is the subject of controversy, but almost certainly is between the limits of 204 and 209 kcal mol^{-1} [12]; this is the major uncertainty in PA(Mn).

Where proton transfer is thermoneutral, proton transfer is expected to occur at about half the collision frequency. This point is indicated in fig. 3, from which $PA(Mn) = 195.5 \pm 2.5$ kcal mol^{-1} is taken. Using $IP(Mn) = 7.43$ eV [18], a metal–hydrogen homolytic bond energy $D^0(Mn^+\text{–}H) = 53 \pm 5$ kcal mol^{-1} is derived. This is compared with other recently determined transition metal–hydrogen bond dissociation energies, $D^0(M^+\text{–}H)$, in table 2 [8,9,19].

Several complications in these experiments deserve comment. Electronically excited transition metal ions are formed in reasonable abundance in the fragmentation of organometallic compounds. These species exhibit enhanced reactivity. In the mixture of formaldehyde with $HMn(CO)_5$, addition of the organic base leads to an increase in the MnH^+ signal which double resonance experiments indicate to come from Mn^+,

$$Mn^+ + CH_2O \rightarrow MnH^+ + HCO . \qquad (4)$$

Table 2

Proton affinities, ionization potentials, metal–hydrogen and metal–methyl homolytic bond energies of transition metal atoms

Metal M	PA(M) (kcal mol^{-1})	IP(M)[a] (eV)	$D^0(M^+\text{–}H)$ (kcal mol^{-1})	$D^0(M^+\text{–}CH_3)$ (kcal mol^{-1})
Mn	196 ±5[b]	7.43	53 ±5[b]	>48 ±5[b]
Fe				62 ±6[c]
Co	184 ±5[d]	7.86	52 ±4[d]	61 ±4[d]
Ni	181 ±2[e]	7.63	43 ±2[e]	

[a] From ref. [18]. [b] This work [c] From ref. [19].
[d] From ref. [8]. [e] From ref. [9].

Continuous ejection of Mn^+ eliminates this contribution, and no increased decay of the MnH^+ signal is observed with added CH_2O ($k < 10^{-11}$ cm^3 molecule^{-1} s^{-1}). Using the above bond energy, reaction (4) is endothermic by ≈37 kcal mol^{-1}. The lowest excited state of Mn^+ with sufficient energy to render process (4) exothermic is a ^5D at 1.78 eV (41 kcal mol^{-1}) [18].

Proton transfer is generally a facile process. In the deprotonation of MnH^+ with sufficiently strong bases this is the only observed reactive pathway. With weak bases the protonation is endothermic, and other reactions may be observed. In the case of CH_3CHO, for example, MnH^+ decays when the neutral base is added to the system, even though no proton transfer is observed. The process

$$MnH^+ + CH_3CHO \rightarrow MnCH_3^+ + H_2 + CO\ , \qquad (5)$$

is identified by double resonance, and a rate constant of 2.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1} is obtained from an analysis of the temporal behavior of ion concentrations. The neutral products are not identified; the only reasonable alternate product in reaction (5) is CH_2O, which has nearly the same heat of formation as H_2 and CO.

The decarbonylation of aldehydes has been observed with other transition metal complexes [20] and atomic ions [21]. The usual process yields the metal carbonyl, via the scheme presented in fig. 4. In the case of MnH^+ the presence of a hydrogen on the metal center allows for the reductive elimination of H_2, presumably before the methyl group transfers to the metal center, as is also shown in fig. 4. As a result, the product $MnCH_3^+$ is observed instead of the carbonyl. Using the derived MnH^+ bond energy, reaction (5) indicates $D^0(Mn^+-CH_3) \geqslant 48 \pm 5$ kcal mol^{-1}. This is in keeping with other reported metal–methyl bond energies, which are given in table 2.

The long time scale of trapped ion ICR experiments makes necessary the consideration that vibrationally or electronically excited ions will relax radiatively; this phenomenon has been observed indirectly in a number of other experiments [22–25]. A major concern here is with the possibility that excited species participate in the observed deprotonation reactions. For an inhomogeneous ion population with varying reactivity, a *non*-linear log plot (of the type shown in fig. 2) would be obtained. In no instance is this observed, and the involvement of excited MnH^+ is ruled out.

It is interesting to compare $D^0(Mn^+-H)$ to the bond energies in related neutral molecules. For main group hydrides, the bond energy in the ion is typically 10–15 kcal mol^{-1} stronger than in the isoelectronic neutral [11]. Our data would indicate that $D^0(Cr-H) \leqslant 53$ kcal mol^{-1}. In addition, combining our data with IP (MnH) would yield the bond energy $D^0(Mn-H)$; this ionization potential has not been reported. A consideration of the electronic structure of MnH [1] indicates the electron lost on ionization is an s–p hybrid somewhat antibonding with respect to the Mn–H bond. This suggests IP(MnH) < IP(Mn), from which it follows that $D^0(Mn-H) < D^0(Mn^+-H) = 53$ kcal mol^{-1}. Gaydon [26] has estimated $D^0(Cr-H) = 66 \pm 12$ kcal mol^{-1} and $D^0(Mn-H) = 55 \pm 7$ kcal mol^{-1}, by using a linear Birge–Sponer extrapolation of the $v = 0$–2 vibrational levels for these molecules. This extrapolation appears to be seriously in error for transition metal hydrides, which is not unexpected considering the major assumptions involved in its use.

4. Conclusion

The present work demonstrates that studies of the kinetics of deprotonation reactions of metal hydride

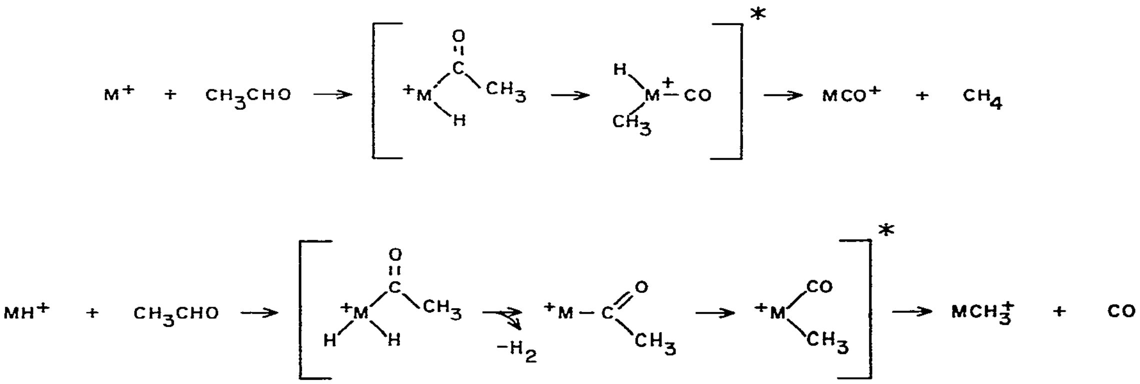

Fig. 4 Mechanism of decarbonylation of aldehydes by transition metal ions, and mechanism of decarbonylation by a transition metal hydride ion.

ions form the basis of an experimental method for the determination of metal atom base strengths and metal–hydrogen bond dissociation energies. This complements other techniques, which include protonation of the neutral metal, an analysis of thresholds for endothermic reactions, and extrapolations of spectroscopic data.

The ion MnH^+ is isoelectronic with CrH and very likely has the same $^6\Sigma^+$ ground state [27]. Deprotonation yields the ^6S ground state of the atom derived from the configuration s^2d^5. The reaction is thus expected to occur on a single electronic surface to yield ground state products. This may contribute to the almost ideal behavior of the MnH^+ system, and is not unexpected for many other metal hydride ions.

Acknowledgement

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