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GAS PHASE ION—MOLECULE REACTIONS OF ORGANOMETALLIC COMPOUNDS; PROTONATION OF η^4 -DIENETRICARBONYLIRON AND η^4 -POLYENETRICARBONYLIRON COMPLEXES BY VARIOUS BRØNSTED ACID REAGENT IONS

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Summary

Gas phase protonation reactions have been investigated between a series of Brønsted acid reagent ions, viz.: H_3^+ , CH_5^+ , $t-C_4H_9^+$, $(NH_3)_nH^+$, and various η^4 -dienetricarbonyliron and η^4 -polyenetricarbonyliron compounds. The protonation reactions and mass spectra are discussed in terms of the relative acid strengths of the protonating reagent ions, and comparisons are drawn between these gas phase results and the conditions necessary to effect protonation of these and similar organometallic compounds in the solution phase.

Introduction

It is now well established that transition metal carbonyls and their derivatives may function as bases in the solution phase and under such conditions may undergo either reversible or irreversible protonation [1–8]. The concept of metal basicity has proved to be useful for the purpose of systematizing many such reactions involving low oxidation state transition metal complexes [2–4]. In addition, acid–base rationalizations have been applied to establish orders of basicity for transition metal organometallic compounds relative to specific reference Lewis or Brønsted acids. Unfortunately, in the solution phase, these reactions are dependent, not only on the solvent, but also on the coordinating ability of the anion of any protonating acid that is being used [6–8]. There have, however, been few attempts to carry out gas phase ion–molecule reactions involving proton transfer to substituted transition metal carbonyls, although the potential of such studies, under solvent free conditions, would seem to be considerable, particularly from the standpoint for systematization of Brønsted acid–base phenomena with selected organometallic compounds.

From a study which is complementary to our investigations of electron attachment to organometallic complexes in the gas phase [9–12], we now report results of proton transfer reactions with a series of η^4 -dienetricarbonyliron and η^4 -polyenetricarbonyliron complexes with the Brønsted acid reagent ions H_3^+ , CH_5^+ (as well as C_2H_5^+ and C_3H_5^+), $\text{t-C}_4\text{H}_9^+$, and $(\text{NH}_3)_n\text{H}^+$ (with $n = 1-3$). These ions may be generated by electron detachment and ion-molecule processes within mass spectrometer ion sources operating at pressures of ca. 1 Torr using as reagent gases, hydrogen, methane, isobutane and ammonia respectively [13,14]. Although proton transfer to a wide range of organic molecules is now routinely performed in the gas phase by recourse to reagent ions of differing acidity [13,14], this, to our knowledge, is the first such attempt at a comprehensive survey in which a range of Brønsted acid reagent ions, of widely different acid strengths [14], has been used to effect proton transfer to a selected series of organometallic compounds. Two earlier papers have given some details of proton transfer to certain organometallic compounds by use only of reagent ions derived from methane [15,16].

Experimental

The η^4 -dienetricarbonyliron complexes used were obtained from Strem Chemicals Inc., Newburyport, Mass., U.S.A., and were purified by trap-to-trap distillation immediately prior to their insertion into the mass spectrometer. They were also characterized from their E.I. positive ion mass spectra. The η^4 -polyenetricarbonyliron complexes were prepared by standard methods [17,18], and were purified either by vacuum sublimation or distillation. The reagent gases which were used for the generation of the Brønsted acid reagent ions were respectively Matheson Gas Products ultra-high purity hydrogen (99.995%); C.P. methane (99.0%); instrument grade isobutane (99.5%); and anhydrous ammonia (99.99%). Proton transfer reactions and mass spectra were effected in and obtained from an AEI MS-902 mass spectrometer fitted with a SRI CIS II high pressure ionization source. Ion source pressures were determined from calibrated thermocouple and ionization gauges located in the source pumping lines, and ion source reagent gas pressures were maintained at ca. 1 Torr, while sample pressures were maintained to minimize the occurrence of sample ion-molecule reactions, according to present standard practices [14]. Both solid and liquid samples were introduced in glass capillaries into the ion source using the solid insertion probe technique. As thermolysis of organometallic compounds is a well recognized phenomenon in heated mass spectrometer ion sources [19], all proton transfer mass spectra were obtained at the minimum practicable ion source temperatures of ca. 100°C, and thermal effects on the spectra were found to be of significance only at temperatures in excess of ca. 160°C. Since the organometallic complexes used in this study contain polyisotopic iron atoms, in some instances the proton transfer mass spectra contained complex clusters of peaks which were composed of species such as $[M + \text{H}]^+$, $[M]^{++}$, $[M - \text{H}]^+$. Elucidation of the contributions of such species to the actual observed clusters was achieved by recourse to comparisons with computer simulated clusters based on normal isotopic distributions.

Results and discussion

Details of proton transfer mass spectra are given in Table 1 for a series of η^4 -dienetricarbonyliron complexes, I–IV, where the diene ligands were respectively cyclobutadiene, 1,3-butadiene, 1,3-pentadiene and 1,3-cyclohexadiene. All significant ions were identified in the mass spectra and the data are presented in terms of the percentages of the total ion current carried by each ion. In addition, fragmentation Scheme 1 has been elucidated as a result of the assignment of metastable peaks, when H_2 was used as the reagent gas, and this Scheme describes the various ion decomposition reactions given by the most significant ions listed in Table 1.

All compounds were protonated by the ions derived from the three reagent gases hydrogen, methane and isobutane. However, even by operating the mass spectrometer under optimized sensitivity and ion detection system gain, no evidence was forthcoming to indicate that ions derived from ammonia, when used as a reagent gas, effected proton transfer to I–IV. We may thus conclude that, at least in the gas phase, these compounds have lower proton affinities than that of ammonia.

For compounds II–IV, the trend towards higher $[M + H]^+$ ion yields, as well as the decreasing degree of fragmentation of these species, parallels the decrease in Brønsted acid strengths of the principal ions effecting protonation. Similar trends are now well recognized features of the proton transfer mass spectra of many organic molecules [15,16]. The yields of $[M]^{2+}$ ions given by I–IV are high, particularly when compared with uncomplexed hydrocarbons where $[M]^{2+}$ is commonly only ca. 5% of $[MH]^+$ [20]. We attribute the presence of $[M]^{2+}$ ions in the spectra to charge exchange reactions [16]. Hydride abstraction reactions which yielded $[M - H]^+$ ions were given by all compounds and reagent gas combinations, although the abundances of such species were low and thus these competing reactions were of lesser significance than either the proton transfer or charge exchange processes.

Scheme 1 outlines the principal ion decomposition reactions given by I–IV, at least when H_3^+ was the protonating acid. Both consecutive and simultaneous decarbonylations of the various ions provide the major ion decomposition path-

SCHEME 1. Fragmentation scheme showing ion decomposition pathways for I–IV, when H_3^+ was the protonating ion.

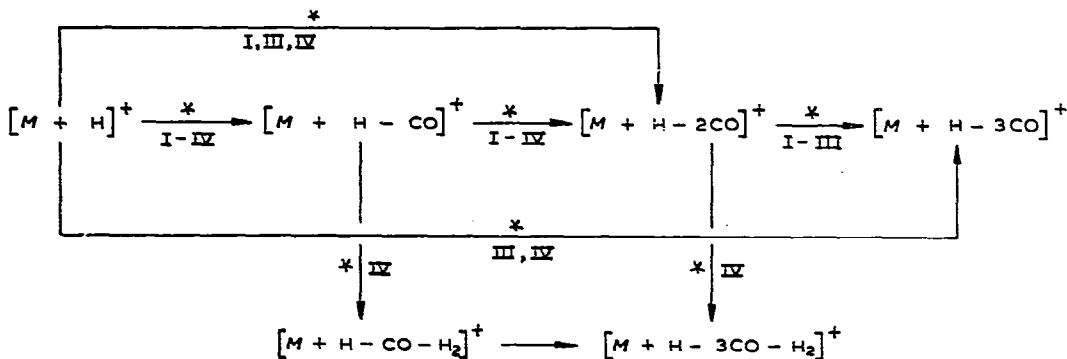


TABLE 1
 PERCENT OF THE TOTAL ION CURRENT CARRIED BY THE SIGNIFICANT IONS IN THE PROTON TRANSFER MASS SPECTRA OF SOME η^4 -CON-
 JUGATED-DIENETRICARBONYLIRON COMPLEXES ^a

Ions	Cyclobutadiene(I)				1,3-Butadiene(II)				1,3-Pentadiene(III)				1,3-Cyclohexadiene(IV)			
	H ₂	CH ₄	i-C ₄ H ₁₀	H ₂	CH ₄	i-C ₄ H ₁₀	H ₂	CH ₄	i-C ₄ H ₁₀	H ₂	CH ₄	i-C ₄ H ₁₀	H ₂ ^c	CH ₄	i-C ₄ H ₁₀	
[M + H] ⁺ (%)	76	78	64	13	21	66	13	33	58	11	44	70				
[M] ⁺	17	11	36	6	15	6	6	10	5	8	9	0.5				
[M - H] ⁺	0.6	0.4	0.2	7	3	0	2	2	0.2	2	1	5				
[M + H - CO] ⁺	5	8	0	54	34	15	57	22	11	8	7	3				
[M - CO] ⁺	0.3	1	0	4	3	2	4	3	1	13	12	2				
[M - H - CO] ⁺	0.4	0.1	0	7	2	0	2	1	0.3	16	25	20				
[M + H - 2CO] ⁺	0.6	1	0	5	14	7	7	8	6	0.3	0.4	0				
[M - 2CO] ⁺	0	0	0	2	1	1	2	4	2	0.3	0.4	0				
[M - H - 2CO] ⁺ b	0	0	0	1	0	0.1	0.3	1	0.5	0.3	0.4	0				
[M + H - 3CO] ⁺	0	0	0	1	3	2	1	3	6	0	0	0				
[M - 3CO] ⁺	0	0	0	1	0.4	1	1	1	1	0.1	0	0				
[M + H - 3CO - H ₂] ⁺	0	0	0	0	<0.1	0	<0.1	1	3	2	0	0				
[M - 3CO - H ₂] ⁺	0	0	0	0	0	0	0	0	0	1	0	0				
[Diene + H] ⁺	0	0	0	1	3	0	5	12	16	0	0	0				

^a Mass spectra were obtained using ionization source temperatures in the range 95-110° C. or [M + H - H₂ - 2CO]⁺, ^c Ion elemental compositions were confirmed by high resolution measurements.

ways, although in the case of IV, minor processes involved the elimination of H_2 from $[M + H - CO]^+$ as well as H_2 and CO from $[M + H - 2 CO]^+$.

It is significant that only for II and III were small yields of protonated diene species observed. These ions were most probably formed by exhaustive elimination of three CO molecules from $[M + H]^+$ followed by demetallation to give, finally, the observed $[DieneH]^+$ ions. The $[DieneH]^+$ yield for II using CH_4 as reagent gas is lower than that given in a previous report [15], and moreover, when a milder protonating reagent ion was used, viz., $t-C_4H_9^+$, no $[DieneH]^+$ was observed with II. Because of the purification techniques used with all compounds prior to their insertion into the mass spectrometer, it is unlikely that residual amounts of free diene ligand impurities could have contributed to the observation of these $[DieneH]^+$ ions.

Although it is not possible to specify with certainty the site of protonation as being either the diene ligand or the metal, some deductions can be made from the data of Table 1. Also, correlations with solution phase protonation studies would seem to be meaningful and provide some insight into possible mechanisms for protonation in the gas phase. Significantly, for I and IV, all ions observed in the mass spectra were metal containing, and for II only very low $[DieneH]^+$ ion yields were given. This provides at least some evidence to suggest that the protonation site was not the diene ligand for I, II, IV. For compound III, higher $[DieneH]^+$ ion yields were given and in this case the inductive influence of the terminal methyl group of the diene ligand could have contributed, at least in part, to diene protonation.

In the solution phase, it is recognized that protonation of η^4 -dienetricarbonyliron complexes can give rise to a variety of reactions that depend very much on the exact reaction conditions employed [4,6-8]. However, for II and IV, at least there is a body of evidence which indicates that protonation results in the formation of monoprotonated metal hydride species which contain a η^3 - π -allyl iron bond [8,21,22]. Recent analysis of $^{13}C-H$ coupling constants has supported the view that the metal hydride moiety may be bridging between iron and carbon in the protonated species [8]. Such a bonding arrangement, were it present in the gas phase $[M + H]^+$ ion, would be expected to allow for the observed decarbonylations from the coordinatively saturated iron atom.

A somewhat different mechanism for protonation could apply for I. Here, significantly, 90% or more of the total ion currents were carried together by $[M + H]^+$ and $[M]^{2+}$ ions. Significantly, too, higher yields of $[M]^{2+}$ ions were given for I compared to the other compounds in this series, which indicates that an alternative process to charge exchange was operative in the formation of these ions. A mechanism similar to that suggested for electrophilic substitution reactions of I may account for these observations [23,24]. In such a mechanism it is envisaged that the proton may interact with the ring to generate a η^3 - π -allyltricarboxyliron cationic species, which, by elimination of H^+ could then yield the observed $[M]^{2+}$ ions, (Scheme 2), rather than undergo fragmentations involving decarbonylations.

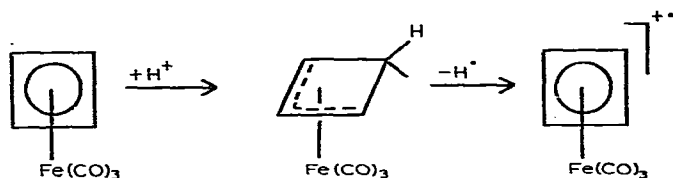
In the case of the η^4 -polyenetricarbonyliron compounds, V-VII, a significantly different electronic situation was presented to the Brønsted acid reagent ions because each molecule possessed at least one uncoordinated carbon-car-

TABLE 2
 PERCENT OF THE TOTAL ION CURRENT CARRIED BY THE SIGNIFICANT IONS IN THE PROTON TRANSFER MASS SPECTRA OF η^4 -POLYENE-TRICARBONYLIRON COMPLEXES^a

Ions	Cycloheptatriene(V)				Cycloheptatrienone(VI)				Cyclooctatetramene(VII)			
	H ₂	CH ₂	i-C ₄ H ₁₀	NH ₃	H ₂	CH ₄	i-C ₄ H ₁₀	NH ₃	H ₂	CH ₄	i-C ₄ H ₁₀	NH ₃
[M + NH ₄] ⁺ (%2)	—	—	—	0	—	—	—	83	—	—	—	0
[M + H]	13	8	53	96	18	20	60	49	1	3	91	80
[M] ⁺	0.1	0.1	0	0	0.1	<0.1	<0.1	0	2	<0.1	0.4	0
[M - H] ⁺	0.6	0.4	4	0	0.4	0.3	0.8	0.1	<0.1	0.1	0.6	0
[M + H - CO] ⁺	29	38	4	1	6	9	4	1	2	4	2	0.6
[M - CO] ⁺	11	19	0	0	3	2	0	0	14	13	5	0
[M - H - CO] ⁺	0.4	0.3	0	0	0.5	0.5	0	0	0.1	0	0.6	0
[M + H - 2CO] ⁺	42	24	11	3	33	44	0	9	31	41	0	10
[M - 2CO] ⁺	2	2	1	0	3	1.2	0	0	2	2	0	0
[M - H - 2CO] ⁺	0.3	0.2	1	0	5	3	0	0	0.1	<0.1	0	0
[M + H - 3CO] ⁺	3	2	9	0.5	23	14	0	6	43	29	0	9
[M - 3CO] ⁺	5	2	2	0	2	0.4	0	0	4	2	0	0
[M - H - 3CO] ⁺	0.7	0.8	3	0	5	2	0	0	0.1	0.5	0	0
[Polyene + H] ⁺	2	3	5	0	3	6	35	0	0.5	5	0	0
[Polyene] ⁺	0	0	0	0	0	0	0	0	0	0	0	0
[Polyene - H] ⁺	2	1	7	0	0	0	0	0	0	0	0	0

^a Mass spectra obtained with ionization source temperatures in the range 100–110°C.

SCHEME 2



bon double bond. From the data presented in Table 2, it can be seen that protonation of V–VII was effected by all reagent ions, while for V and VII, increasing yields of $[M + H]^+$ resulted as the Brønsted acid strength of the protonating ions decreased from H_3^+ to $(NH_3)_nH^+$. The proton affinities of V–VII can therefore be concluded to be greater than that of ammonia. However, for VI, a competing reaction which gave a significant yield of $[M + 18]^+$, that is the $[M + NH_4]^+$ species, may be ascribed to an electrophilic attachment process involving the interaction of NH_4^+ reagent ions with the carbonyl function of the 2,3,4,5- η^4 -cycloheptatrienone ligand. Similar electrophilic attachment reactions involving this reagent ion and uncoordinated ketone molecules are well documented [25].

Very low yields of $[M]^{++}$ as well as $[M - H]^+$ ions for V–VII indicated that charge exchange as well as hydride abstraction processes were of minimal significance, although the presence of $[M - n CO]^{++}$ ions in the spectra, which derived from $[M]^{++}$ ions indicated that some degree of electron ionization of M had occurred in each case. Elucidation of the principal ion decomposition pathways by metastable defocusing indicated that sequential decarbonylations of the $[M + H]^+$ ions occurred in all cases, viz.: $[M + H]^+ \rightarrow [M + H - CO]^+ \rightarrow [M + H - 2 CO]^+ \rightarrow [M + H - 3 CO]^+$.

There is available a considerable amount of solution phase protonation data for V–VII [4,6,26,27] which, in the main, relate to studies which have been carried out in strongly acidic media, and in addition, one earlier report has given some details of the gas phase protonation of VI and VII, by use only of CH_4 as the reagent gas [15]. Perhaps the most significant feature that emerges from the present study is that in the gas phase very mild protonating conditions using the weak Brønsted acid ions $(NH_3)_nH^+$ are sufficient to form high yields of $[M + H]^+$ for V and VII, and the necessary requirement for this reaction is that the proton affinity of the compounds be greater than that of ammonia, viz., 840 kJ mole^{-1} [14]. Although the site of protonation for VI and VII may well have been at the uncoordinated double bonds of the polyene ligands, as has been established from solution phase protonation studies [26,27], it is noteworthy that in general only low yields of $[PolyeneH]^+$ ions were obtained, and that the major proportions of the total ion currents were carried by metal-containing ions. Use of ND_3 as a reagent gas is now being attempted in an endeavour to establish with greater certainty protonation sites with these and other organometallic compounds.

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