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Dinitrogen addition to c-$C_5H_5Fe^+$, $C_6H_6Fe^+$ and FeO^+ in the gas phase

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Abstract

Results of an experimental study using the selection-ion flow tube technique are reported for reactions of bare Fe^+ and iron containing FeX^+ cations ($X = C_6H_6$ (or B), c-C_5H_5 (or Cp), O, $(Cp)_2$, B_2) with dinitrogen at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. Fe^+, B_2Fe^+ and Cp_2Fe^+ do not react with dinitrogen. A very slow sequential addition of two N_2 molecules was observed with FeO^+. $CpFe^+$ and BFe^+ reacted without the subsequent addition of a second N_2 molecule. These results provide insight into the bonding of N_2 as a ligand with Fe as the coordination centre in the gas-phase, and into intrinsic kinetic aspects of dinitrogen addition.

Iron is the only transition metal common to all biological systems of dinitrogen fixation [1,2]. Recent experimental and theoretical studies [3–11] of transition metal cation–dinitrogen and other small ligand complexes in the gas-phase have found that the binding energies of these complexes are much larger than theoretical values based on electrostatic bonding alone. It has been shown that charge transfer/charge-quadrupole interaction and covalent bonding are also important [4–7]. We present here the first experimental evidence for the coordination of unsaturated FeX^+ cations, in particular c-$C_5H_5Fe^+$ ($CpFe^+$), $C_6H_6Fe^+$ (BFe^+) and FeO^+ with dinitrogen as a ligand to iron in the gas-phase at 294 ± 3 K. Also, kinetic measurements are reported here which provide the first insight into the *intrinsic efficiency* of dinitrogen addition reactions.

The results reported here (see Table 1) were obtained using a selected-ion flow tube (SIFT) which has been described previously [12,13]. All measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. The reactant cations Fe^+, $CpFe^+$ and Cp_2Fe^+ were produced in a low pressure ionization source by 20–70 eV electron-impact ionization of Cp_2Fe vapour. In the experiments with BFe^+ and B_2Fe^+ cations were produced from Fe^+ all the way upstream in the flow tube by adding benzene (1.1×10^{17} molecule s^{-1}) through the aspirator gas inlet together with the helium buffer gas. FeO^+ was derived from the reaction $Fe^+ + N_2O \rightarrow FeO^+ + N_2$ in a mixture of $Fe(CO)_5$ and N_2O in a high-pressure ionization source. All the regent cations were allowed to thermalize upstream of the flow tube by $\approx 4 \times 10^4$ collisions with He atoms before adding N_2.

The adduct complexes BFe^+ and $CpFe^+$, which have a pyramidal structure [14,15], were observed to react with dinitrogen and formed adducts without the subsequent addition of a second molecule of N_2. Rate coefficients are summarized in Table 1 and a

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Table 1
Rate coefficients [a] for selected reactions between Fe^+-containing ions and N_2 at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr

Ion	k_{obs} [b]	k_{cap} [c]	$k(3)_{obs}$ [d]
Fe^+	$< 10^{-14}$	7.15×10^{-10}	$< 9 \times 10^{-31}$
FeO^{+c}	5.0×10^{-14}	6.88×10^{-10}	4.4×10^{-30}
$FeO(N_2)^+$	$\leqslant 1.5 \times 10^{-14}$	6.60×10^{-10}	$\leqslant 1.3 \times 10^{-30}$
$FeO(N_2)_2^+$	$< 10^{-14}$	6.45×10^{-10}	$< 9 \times 10^{-31}$
$CpFe^+$	2.2×10^{-11}	6.48×10^{-10}	1.9×10^{-27}
$CpFe(N_2)^+$	$< 10^{-14}$	6.36×10^{-10}	9×10^{-31}
$(Cp)_2Fe^+$	$< 10^{-14}$	6.26×10^{-10}	9×10^{-31}
BFe^+	1.5×10^{-11}	6.41×10^{-10}	1.3×10^{-27}
$(B)_2Fe^+$	$< 10^{-13}$	6.21×10^{-10}	$< 9 \times 10^{-31}$
B^+	$< 10^{-13}$	6.90×10^{-10}	$< 9 \times 10^{-31}$

[a] All bimolecular rate coefficients are in units of cm^3 $molecule^{-1}$ s^{-1}.
[b] Measured effective bimolecular reaction-rate coefficient. The absolute error may be as high as ±30%, but the relative error is lower than 5%.
[c] The collision rate coefficient was calculated according to the ADO method described by Su and Bowers [31].
[d] Termolecular rate coefficient, in units of cm^6 $molecule^{-2}$ s^{-1}, calculated from k_{obs}.
[e] The association with CO impurities could be excluded due to the reaction $FeO^+ + CO \rightarrow Fe^+ + CO_2$.

reaction profile is shown in Fig. 1. We believe that the observed $BFe(N_2)^+$ and $CpFe(N_2)^+$ cations were formed under our experimental conditions by termolecular association with He atoms stabilizing their body (the termolecular rate coefficients calculated from k_{obs} are shown in Table 1). Also radiative stabilization is able to play a certain role in the stabilization of observed complexes but the effective bimolecular rate coefficients, the reaction time and the small number of atoms in the intermediate complex rule out radiative stabilization as a significant alternative association mechanism [16,17]. The rate coefficients for $CpFe^+$ and BFe^+ reveal that the internal degrees of freedom of the cyclopentadienyl/benzene-carbocycles are not significantly involved in the complexation energy dispersal. $BFe(N_2)^+$ has more degrees of freedom (a longer lifetime if the binding energies are similar) as compared to $CpFe(N_2)^+$; the intrinsic reaction efficiency of N_2 addition to BFe^+ is found to be lower than that for $CpFe^+$. Since this difference cannot be attributed to an increase in degrees of freedom alone, the large rate coefficients in the case of $CpFe(N_2)^+$ formation imply a bond stronger than that in $BFe(N_2)^+$.

What is the nature of the bonding in $CpFe(N_2)^+$ and $BFe(N_2)^+$? The failure to observe significant reactions between N_2 and B^+, B_2Fe^+ and Cp_2Fe^+ ions is strong evidence that iron is the reaction center in the reactions of BFe^+ and $CpFe^+$. In order to form a 6π-electron complex with $C_5H_5^-$, iron donates one electron and the formal oxidation number of Fe in $CpFe^+$ is equal to two. Benzene already has the aromatic 6-electron configuration and iron in $BFe(N_2)^+$ has a lower local positive charge. Fe in $CpFe^+$ is 0.52 e^- more deficient than the Fe^+ centre in BFe^+ [14]. Our experimental observations are consistent with an explicit bond energy analysis [4] which shows that the charge/induced dipole and

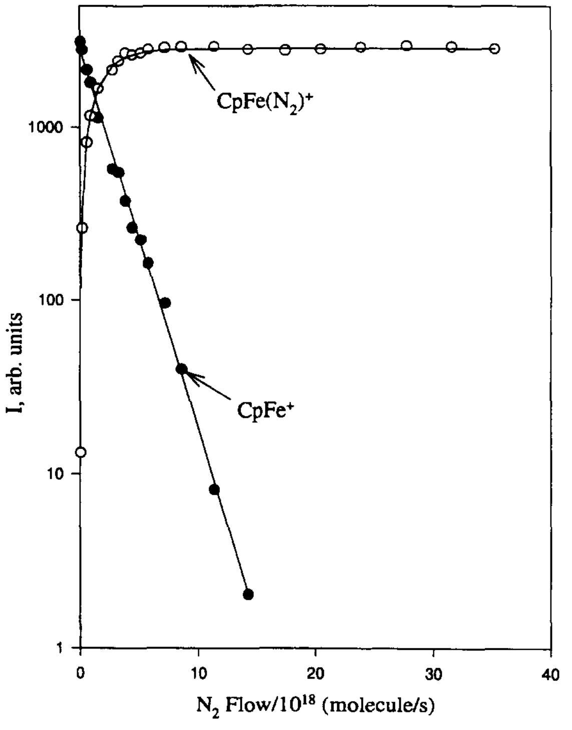

Fig. 1. Experimental data for the reaction of $CpFe^+$ with N_2. The measurements were performed at 294 ± 3 K and at a helium buffer-gas pressure of 0.35 ± 0.01 Torr. $CpFe^+$ was formed initially by 55 eV electron-impact dissociative ionization of Cp_2Fe vapour. The solid lines represent a fit to the experimental data with the solution of the system of differential equations appropriate for the observed reactions. Rate coefficients derived from this fit are given in Table 1.

charge/quadrupole interactions account for more than 75% of the total bond energy in the Cr^+/Co^+-N_2 complexes. Additional contributions are short-range electronic repulsion and charge transfer. This type of bonding in weakly bound organometallic systems greatly depends on the metal local charge and should be stronger in the $CpFe(N_2)^+$ complex. We suggest that cyclopentadienyl and benzene have electronic properties as co-ligands which can contribute to the stability of the dinitrogen–metal complexes as a consequence of $Fe \rightarrow N_2$ π acceptance [18,19] [1]. Some compounds containing π-electron donating ligands such as $Cp(CO)_2Mn(N_2)$ [20] and also mixed dinitrogen cyclopentadienyl-phosphine, THF, benzyl complexes of Zr, Li, Ir [21–25] are known.

Iron in FeO^+ has a higher local positive charge [26] than iron in BFe^+ and $CpFe^+$, and should exhibit the strongest bond with N_2 among all the complexes considered in this study. We observed a slow addition of *two* N_2 molecules to the FeO^+ cation which is more consistent with a higher contribution of charge-induced dipole, quadrupole/charge transfer bonding in comparison with $CpFe^+$ and BFe^+. However, the experiment reveals that FeO^+ reacts with dinitrogen at least 100 times slower. This difference in reactivity can be rationalized in terms of a difference in the collision-complex life time which is influenced not only by the FeX^+-N_2 bonding energy but also by the number of active vibrational modes in the collision complex. The FeX^+-N_2 complex has more than 5 active modes (assuming that dinitrogen rotational and translational modes were converted into active vibrational modes). In this case only 1–3 additional modes need to be active in $CpFe^+$ and BFe^+ in order to explain the more than two order of magnitude difference in the rate coefficients.

The reaction between dinitrogen and bare iron cation was also investigated in our laboratory. Strictly speaking this reaction cannot be directly compared with the addition of N_2 to FeX^+ complexes. The Fe^+ ion in the ^6D ground state ($4s^13d^6$) has a large 4s orbital which contributes in repulsive interaction with dinitrogen. A similar interaction is absent in the electronic ground states for $CpFe^+$ ($^5E_2$) [14] and BFe^+ ($^4A_2$) [15]. The failure to observe addition of N_2 to Fe^+ can be explained by a short lifetime of the intermediate Fe^+-N_2 complex which may arise from weak bonding and/or a small number of degrees of freedom effective in energy dispersal.

It seems surprising, at first glance, that $CpFe^+$ and BFe^+ form only one adduct with dinitrogen. We were unable to observe addition of a second and third molecule of N_2 to $CpFe(N_2)^+$ and $BFe(N_2)^+$ ions even at high flow of dinitrogen (up to 10^{19} molecule/s). In contrast, other experiments in our laboratory have shown that $CpFe^+$ rapidly adds up to three CO and up to two NO molecules under similar experimental conditions [27]. This allows us to rule out steric effects in the formation of the bis/multi(dinitrogen) complexes. It is interesting to note that the addition of more than one molecule of N_2 to mononuclear transition metal complexes is also very rare in condensed phase chemistry [21,22]. However, half-sandwich complexes containing d^6 transition metal centers bonded to more than one N_2 molecule such as $CpRe(CO)(N_2)_2$, $CpRe(N_2)_3$ and $(c\text{-}C_4H_4)Fe(CO)(N_2)_2$ have been synthesized under cryogenic conditions [9] and in supercritical fluids [11]. The latter experiments were conducted using supercritical Xe doped with N_2 at extremely high pressure. The pressure used in our gas-phase experiments is less by more than 6 orders of magnitude. Moreover, the bis/multi(dinitrogen) complexes observed in supercritical fluids were volatile and always in low concentrations. Taken together, all of these results indicate that the first metal–dinitrogen bond in $CpFe(N_2)^+$ and $BFe(N_2)^+$ is especially strong compared with second- and higher-order bonds.

Can we understand the structures of the adducts which we have observed? It is known that for mononuclear metals end-on η^1 bonding is most common [4,5], although η^2 side-on bonding (via dinitrogen π bonds, as with alkenes) has also been reported [21–23,28–30]. Scheme 1 shows the two possible types of bonding to dinitrogen as a ligand in the $CpFe(N_2)^+$ complex. Iron in $CpFe^+$ has three available d orbitals for dinitrogen end-on bonding which theory says requires two d orbitals [21]. Side-on

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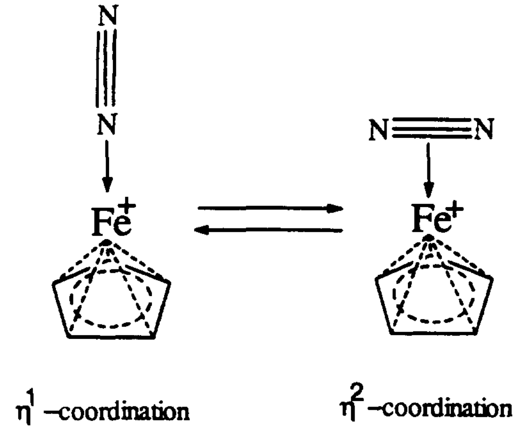
[1] For the influence of the presence of other ligands on the metal–ligand binding energy see Ref. [19].



Scheme 1.

coordination exists in the condensed phase for similar systems only as an intermediate in end-to-end rotation [4,5,27]. The remaining one d orbital around ion in $CpFe(N_2)^+$ is not sufficient for the bonding of a second dinitrogen and so for the formation of $CpFe(N_2)_2^+$. This is a possible explanation for the absence of $CpFe(N_2)_2^+$ in our experiments as well as in the condensed phase.

Although a strong σ interaction may force the dinitrogen initially into side-on bonding in the base of the iron oxide ion [21], end-on configuration is likely to prevail due to the dominant charge/induced dipole and charge/quadrupole interactions [4,5]. The high positive charge on the iron in $FeO(N_2)^+$, the absence of steric limitations and the tendency to fill the still incomplete valence shell allow $FeO(N_2)^+$ to attach another dinitrogen, as was observed in our experiments.

The gas-phase results obtained in this study open a new field of investigations of intrinsic kinetic and mechanistic aspects of dinitrogen addition. Further investigations in the gas-phase extended over a wider range of ligands and transition metals, and to ligand switching reactions, should significantly improve our understanding of fundamental aspects of dinitrogen addition and so have an impact on condensed-phase chemistry. For example, from what we have learned in this study, we expect that some organometallic salts of $CpFe^+$ may reveal a dinitrogen addition reaction similar to that observed by us in the gas-phase.

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