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Distinction of Fe^+-NCH and Fe^+-CNH Complexes by Gas-Phase Ion-Molecule Reactions

Detlef Stöckigt and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, F.R.G.

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The bond dissociation energies and the heats of formation of the complexes Fe^+-NCH (**6**) and Fe^+-CNH (**10**) have been determined. The HCN ligand in **6** is by 3 kcal/mol less strongly bound to Fe^+ than HNC in **10**, and complex **6** is 13 kcal/mol more stable than **10**. Isomerization of **10** to **6** is difficult if not impossible to bring about as, upon collisional activation, mutual isomerization cannot compete with ligand detachment. In addition, the ion-molecule reactions of **6** and **10** with O_2 give rise to distinct product distributions.

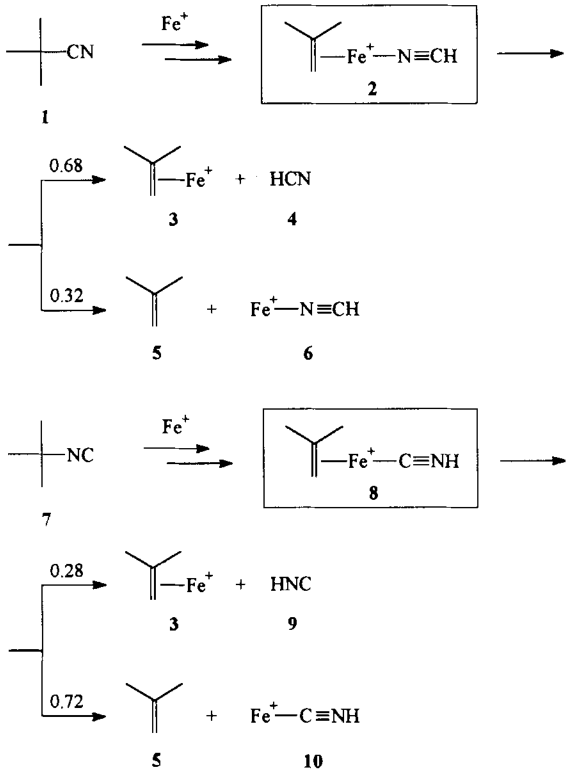
As demonstrated earlier[1] the gas-phase chemistry of *tert*-butyl cyanide (**1**) and *tert*-butyl isocyanide (**7**) with "bare" Fe^+ is characterized by the formation of the ion-dipole complexes **2** and **8**, respectively (Scheme 1). These intermediates owe their existence to a highly specific sequence of elementary steps: Initial "end-on" complexation of the functional groups X (X = CN, NC) is followed by (i) a cleavage of the C–X bond and (ii) and intracomplex proton transfer from the incipient t-$C_4H_9^+$ ion to the XM dipole to generate **2** and **8**. These complexes serve as precursors of the products depicted in Scheme 1, and high-energy collision experiments provided evidence that the [Fe, H, N, C]$^+$ ion generated from cyanide **1** does indeed correspond to the complex Fe^+-NCH (**6**); when the process starts from isocyanide **7**, the isomeric form Fe^+-CNH (**10**) is generated.

In this paper the following three aspects will be addressed: (i) We will report on the bond dissociation energies (BDEs) and heats of formation (ΔH_f) of **6** and **10**. (ii) It will be demonstrated that **6** and **10** do not only exhibit a different behavior when subjected to high-energy collisional activation[1]; the gas-phase reactions of **6** and **10** with molecular oxygen at thermal energies are also quite distinct. (iii) Preliminary experiments are described aimed at an attempted collisional isomerization of **10** to **6** using the SORI (sustained off-resonance isomerization) technique[2]. All experiments were conducted by means of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, employing a Spectrospin CMS 47X instrument, which is equipped with an external ion source; the instrument and details of its operation have been previously described[1b,3,4].

The bond dissociation energies of Fe^+-NCH (**6**) and Fe^+-CNH (**10**) were determined on the basis of the ligand exchange process defined in Eq. (1). From the occurrence versus non-occurrence (bracketing method)[11] of the reaction, lower and upper borders of BDE are available using the literature-known BDE(Fe^+-L')[12].

$$Fe^+-L + L' \rightarrow Fe^+-L' + L \qquad (1)$$

Scheme 1



From the data given in Table 1 and ref.[12] for the complex Fe^+-NCH (**6**) we obtain 34 < BDE(Fe–NCH) < 37 kcal/mol; for the isomer Fe^+-CNH (**10**) the bond dissociation energy amounts to 37 < BDE(Fe^+-CNH) < 40. In line with the previously reported[1a,11a] thermochemical properties of the Fe^+[1a] and $NiCp^+$[11a] complexes of CH_3CN and CH_3NC, the present finding suggests

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that the RCN ligand (R = H, CH_3) is generally less strongly bound than RNC to Fe^+; this may well reflect the stronger σ-donor and π-acceptor capabilities of the RNC in comparison with the RCN ligands. Similar results are predicted by qualitative MO theory to hold true for *neutral* metal fragments as well[14], and adsorption studies of RCN and RNC on Ni surfaces reveal an analogous trend[15]. From the BDEs of **6** and **10** together with the thermochemical data compiled in Table 2, the heats of formation of **6** and **10** can be derived, and we obtain: $\Delta H_f(\mathbf{6}) = 278 \pm 10$ kcal/mol, $\Delta H_f(\mathbf{10}) = 291 \pm 10$ kcal/mol. These data together with the heats of formation of the remaining products shown in Scheme 1 lend further support to our explanation used previously[1a] to explain the branching ratios reported in Scheme 1: As the binding energy of HCN to Fe^+ is smaller than that of HNC and neutral HCN is more stable than HNC (by at least 10 kcal/mol[16]), intermediate **2** should prefer to dissociate to the pair **3/4** rather than **5/6**; in contrast, for **8** the preferred decomposition channel should lead to the formation of **5/10** rather than **3/9**. This is precisely corroborated by the experimental results (Scheme 1).

Table 1. Comparison of the experimental (k_r) and calculated (k_{coll}) rate constants for the ligand exchange process $Fe^+{-}L + L' \rightarrow Fe^+{-}L' + L$[a]

L	L′	k_r[b]	k_{coll}[c]	k_r/k_{coll}
HCN	C_2H_4	[d]		
	C_3H_6	12	11.9	1.0
	i-C_4H_8	13	12.8	1.0
	CH_3CN	40	35.9	1.1
HNC	C_2H_4	[d]		
	C_3H_6	[d]		
	$H^{13}CN$	[d]		
	i-C_4H_8	12	12.8	0.9
	CH_3CN	41	35.9	1.1
C_2H_4	HCN	30	31.2	0.9
C_3H_6	HCN	[d]		
i-C_4H_8	HCN	[d]		

[a] All rate constants are given in units of 10^{-10} $cm^3 \cdot molecule^{-1}\, s^{-1}$. – [b] The estimated error of k_r is ±25%[13]. – [c] The collision rate constant k_{coll} was calculated according to ref.[17]. – [d] Rather than ligand substitution we observe the formation of association complexes $Fe(L')L^+$.

Table 2. Heats of formation (ΔH_f) in kcal/mol used to evaluate thermochemical data[a]

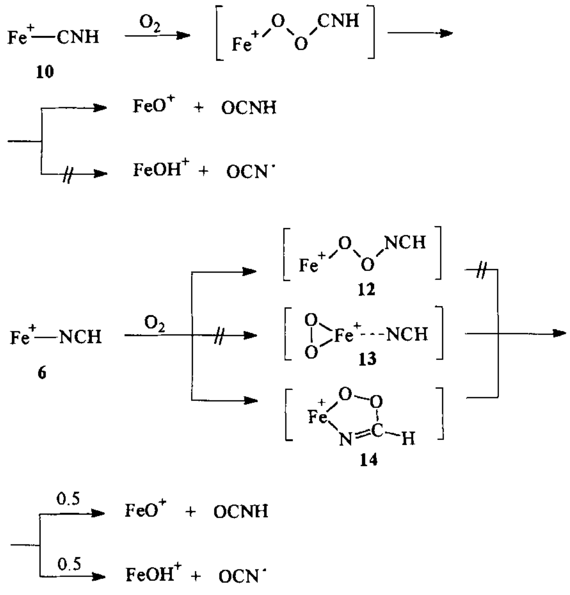
Neutral	ΔH_f	Ion	ΔH_f
$CN^\bullet$	104	Fe^+	281
HCN	32	FeO^+	266
HNC	48	$FeOH^+$	211
$NCO^\bullet$	37	$Fe(HCN)^+$ (**6**)	278[e]
$CNO^\bullet$	104[b]	$Fe(HNC)^+$ (**10**)	291[c,e]
$CON^\bullet$	177[b]		
HNCO	−25		
HCNO	53[c]		
HOCN	−2[c]		
HONC	66[c]		
i-C_4H_8	−4		
t-C_4H_9CN	−1		
t-C_4H_9NC	21[d]		

[a] All data are taken from ref.[19] if not stated otherwise. – [b] Estimated value based on data given in ref.[20]. – [c] Taken from ref.[21]. – [d] Estimated value based on the known ΔH_f data of CH_3CN and CH_3NC[26]. – [e] This work.

In order to exclude the possible existence of barrier in the ligand exchange processes (Eq. 1), we have determined the rate constants k_r for the reactions of interest and compared k_r with the calculated collision rate constants k_{coll}[17]. As indicated by the data in Table 1, if ligand exchange takes place it always proceeds with collision rate. This observation lends further credibility to our approach of determining the BDE by using the bracketing method[11,18].

While both **6** and **10** react with O_2 at thermal energies with collision rate, the product distribution differs (Scheme 2). From the latter complex $Fe^+{-}CNH$ (**10**), the only ionic product observed corresponds to FeO^+, while the isomeric species $Fe^+{-}NCH$ (**6**) gives rise to a 1:1 mixture of FeO^+ and $FeOH^+$. Obviously, interconversion of the two isomers does not take place in the course of the ion-molecule reactions. Thermochemical considerations (Table 2) suggest that the neutral HNCO cogenerated in the oxidation of **10** most likely corresponds to isocyanic acid. The reaction may involve the peroxo complex **11**, which can decompose directly to FeO^+ and HNCO. Although dissociation of **11** to $FeOH^+$ and $NCO^\bullet$ is also exothermic, from the non-occurrence of this process we infer the existence of a kinetic barrier for the *intra*molecular hydrogen transfer. If a direct insertion of O_2 is also operative for $Fe^+{-}NCH$ (**6**) to produce **12**, on thermochemical grounds intermediate **12** cannot dissociate directly to FeO^+ and fulminic acid (HCNO). In order to make the oxidation of **6** exothermic, rearrangement must precede dissociation, and this view is also supported by the formation of the rearrangement products $FeOH^+$ and presumably $NCO^\bullet$. While the nature of the neutral species cogenerated in ion-molecule reactions remains – on principal grounds – undetermined, thermochemical data rule out that $CNO^\bullet$ or $CON^\bullet$ are accessible in the oxidative formation of $FeOH^+$ from **6**. We cannot presently offer a plausible mechanism for the reaction of $Fe^+{-}NCH$ (**6**) with O_2. However, among the many conceivable intermediates, initial replacement of HCN by O_2 to generate the ion-dipole complex **13** is unlikely n view of the fact that BDE($Fe^+{-}O_2$) < BDE($Fe^+{-}NCH$)[22]. Quite attractive, though purely speculative, is the idea of a cycloaddition reaction to first generate **14**, which may then serve as an intermediate for the skeletal rearrangements. Obviously, further work is indicated to elucidate the mechanistic details of the oxidations of **6** and **10**.

Scheme 2



The last aspect concerns the possibility of a mutual interconversion of the Fe^+ complexes **6** and **10** upon collisional activation. For the metal-free systems, i.e. HCN and HNC, there is now ample

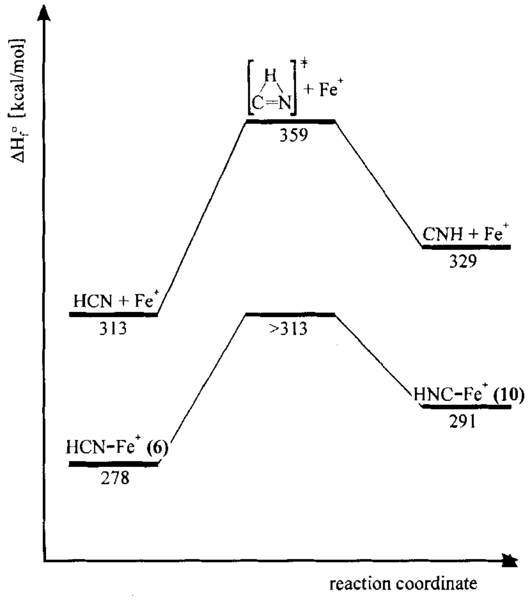


Figure 1. Schematic potential energy surfaces for the isomerizations HCN ⇄ HNC and $HCN-Fe^+$ ⇄ $HNC-Fe^+$; for the sake of clarity, in the HCN/HNC system the heat of formation of *uncomplexed* Fe^+ is included

evidence that the barrier for the isomerization of HNC to HCN is quite high (>30 kcal/mol)[16b], thus explaining that the two species are indeed viable in the gas phase. For the Fe^+ complexes, there is not even semiquantitative information available as to whether ligand detachment, i.e. loss of HCN from **6** or HNC from **10**, energetically predominates over the exothermic isomerization **10** → **6**. The latter, of course, is likely to be a multistep process, whose details are presently studied computationally[23]. We have applied the SORI technique[2] to the complex Fe^+–CNH (**10**) by irradiating **10** with an off-resonance radio frequency pulse over a period of 0.5–2 s in the presence of argon (which serves as a collision partner). Over the whole energy regime (E_{lab} = 18–40 eV) the only product observed corresponds to Fe^+. When the collisionally excited complex **10**, which had not absorbed enough energy to dissociate, reacts with O_2, we observe exclusive formation of FeO^+. The $FeOH^+$ species which would be indicative of the presence of **6** (see Scheme 2) is not generated. Thus, isomerization of **10** to **6** requires a higher activation energy than the lowest dissociation channel. From the data given in Table 2 one can construct an oversimplified potential energy surface (Figure 1), according to which the barrier for the multistep isomerization **10** → intermediates → **6** exceeds 22 kcal/mol. This result supports previous, less direct observations[24] that a metal-ion-mediated isomerization of the type RNC → RCN is not a facile process..

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[1] [1a] K. Eller, H. Schwarz, *Organometallics* **1989**, *8*, 1820. – [1b] K. Eller, W. Zummack, H. Schwarz, *J. Am. Chem. Soc.* **1990**, *112*, 621.

[2] [2a] J. W. Gauthier, T. R. Trautman, D. B. Jacobson, *Anal. Chim. Acta* **1991**, *246*, 211. – [2b] R. Bakhtiar, C. M. Holznagel, D. B. Jacobson, *Organometallics* **1993**, *12*, 621.

[3] [3a] K. Eller, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. – [3b] K. Eller, Ph. D. Thesis, Technische Universität Berlin, **1991**, D83.

[4] Briefly, Fe^+ ions were generated by laser desorption/ionization[5] by focussing the beam of an Nd:YAG laser (Spectron Systems: λ = 1064 nm) onto a stainless-steel target, which is affixed in the external ion source. The ions are extracted from the source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (Balzers TPU 330 for source and cell and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of a superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.0 T. The metal's most abundant isotope is isolated by using FERETS[6]. For collisional cooling of any excited states possibly formed, argon was present as a buffer gas at a constant "background" pressure of ca. 5×10^{-7} mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). For SORI[2] and CID (collision-induced dissociation experiments)[7] argon or helium were employed. For the generation of the $[Fe,H,C,N]^+$ complexes **6** and **10**, the cyanide and isocyanide precursors **1** and **7** were introduced through a leak valve at a constant pressure of ca. 5×10^{-9} mbar. The FeL^+ complexes (L = C_2H_4, C_3H_6, i-C_4H_8, and CH_3CN) have been synthesized as described earlier[8]. For the ion-molecule reactions of **6** and **10** with O_2, oxygen was diluted with argon (1:10) and was pulsed in as described earlier[9]. All complexes were isolated by double-resonance ejection, and great care was applied to avoid any off-resonance excitation of the ion of interest while ejecting the ^{13}C-isotope signals[10].

[5] R. B. Cody, R. C. Burnier, W. D. Reents, Jr., T. J. Carlin, D. A. McCrery, R. K. Lengel, B. S. Freiser, *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 37.

[6] R. A. Forbes, F. H. Laukien, J. Wronka, *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

[7] R. B. Cody, B. S. Freiser, *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199.

[8] D. Stöckigt, S. Sen, H. Schwarz, *Chem. Ber.* **1993**, *126*, 2553.

[9] T. J. Carlin, B. S. Freiser, *Anal. Chem.* **1983**, *55*, 571.

[10] [10a] J. L. Beauchamp, *Ann. Rev. Phys. Chem.* **1971**, *22*, 527. – [10b] A. J. R. Heck, L. J. de Koning, F. A. Pinkse, N. M. M. Nibbering, *Rap. Commun. Mass Spectrom.* **1991**, *5*, 406.

[11] [11a] R. C. Corderman, J. L. Beauchamp, *J. Am. Chem. Soc.* **1976**, *98*, 3998. – [11b] B. S. Freiser, *Chemtracts – Anal. Phys. Chem.* **1989**, *1*, 65.

[12] The BDE(Fe^+–L') relevant in the present context are as follows: C_2H_4: 34 kcal/mol; C_3H_6: 37 kcal/mol; i-C_4H_8: 40 kcal/mol; CH_3CN: 42 kcal/mol. All data were taken from ref.[13], and the literature quoted therein.

[13] D. Schröder, Ph. D. Thesis, Technische Universität Berlin, **1993**, D83.

[14] J. A. S. Howell, J.-Y. Saillard, A. Le Beuze, G. Jaouen, *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

[15] C. M. Friend, J. Stein, E. L. Muetterties, *J. Am. Chem. Soc.* **1981**, *103*, 767.

[16] [16a] G. Frenking, H. Schwarz, *Naturwissenschaften* **1982**, *69*, 446. – [16b] W. Koch, G. Frenking, H. Schwarz, *Naturwissenschaften* **1984**, *71*, 473, and references cited therein. – [16c] For a recent, time-dependent quantum study of the HCN → HNC isomerization see: B. L. Lau, J. M. Bowman, *J. Phys. Chem.* **1993**, *97*, 12535.

[17] T. Su, W. J. Chesnavich, *J. Chem. Phys.* **1982**, *76*, 5183.

[18] D. Thölmann, Ph. D. Thesis, Universität Bielefeld, **1992**.

[19] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[20] W. Koch, G. Frenking, *J. Phys. Chem.* **1987**, *91*, 49.

[21] [21a] J. H. Teles, G. Maier, B. A. Hess, Jr., L. J. Schaad, M. Winnewisser, B. P. Winnewisser, *Chem. Ber.* **1989**, *122*, 753. – [21b] K. Yokoyama, S. Takane, T. Fueno, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2230.

[22] D. Schröder, A. Fiedler, J. Schwarz, H. Schwarz, submitted for publication in *Inorg. Chem.*

[23] W. Koch, M. Holthausen, unpublished results.

[24] K. Eller, C. B. Lebrilla, T. Drewello, H. Schwarz, *J. Am. Chem. Soc.* **1988**, *110*, 3068.

[407/93]