Space Catalysis from Transition Metals? An Astrochemical Journey

Marco Fioroni

Konrad Müller Str. 17, 52249, Eschweiler, Germany

E-mail: `mfioroni@lycos.com`

Abstract. Transition Metals (TM) are proposed to play a role in astrophysical environments in both gas and solid state astrochemistry by co-determining the homogeneous/heterogeneous catalysis represented by the gas/gas and gas/dust grain interactions. Their chemistry is function of temperature, radiation field and chemical composition and, as a consequence, dependent from the astrophysical object in which the TM are localized, *i.e* interstellar medium (ISM), molecular clouds, hot cores and *corinos*. Five main categories of TM compounds classified as: **a)** pure *bulk* and clusters; **b)** TM naked ions; **c)** TM oxides/minerals or inorganic; **d)** TM-L (L = ligand) with L = (σ and/or π)-donor/acceptor species like H/H_2, N/N_2, CO, H_2O and **e)** TM-organoligands such as C_p, PAH, $R_1{=}\bullet{=}\bullet{=}R_2$ are proposed. Such variety of TM compounds opens the door to an enormous potential contribution to a *fine astrochemical synthesis*. Particular attention and interest has been applied to the chemistry of simple TM compounds with general formula: $[\mathrm{TM}_m X_y]^{+n}$ with +n=total charge and X = non-TM element. Constraining the TM and the X elements on the basis of their reciprocal reactivity and cosmic abundances, the chemistry of TM = Fe coupled with N, O, S open the pathway to the correlated organic chemistry. In particular the chemistry of the iron molecular oxide $[\mathrm{FeO}]^{+1}$ and nitride $[\mathrm{FeN}]^{+1}$ will be analyzed, due to their ability to perform C-C and C-H bond activations, opening the pathway to the oxydation/hydroxylation and nitrogenation/amination of organic substrates contributing, for example, to explain the detected presence of NH, NH_2 and CH_3OH in diffuse gas, where actual gas-phase and grain surface chemical models cannot adequately explain the data. Summarizing the TM fine chemistry is expected to contribute to the known synthesis of organic compounds leading towards a new path in the astrochemistry field whose qualitative (type of compounds) and quantitative contribution must be unraveled.

Keywords: Cosmochemistry, Astrochemistry, Transition Metals Genesis, Organometallics, Catalysis

1. Introduction

1.1. The Chemistry Age

The Universe can be seen as an immense heterogeneous non-equilibrium chemical reactor of which richness, variety and complexity can still surprise a curious Scientist. The aforementioned definition of Universe however must be developed by differentiating it from what would be a simple type of *industrial heterogeneous non-equilibrium chemical reactor* by underlining the latest developments on its evolution and constitution analysis. The measurements of the CMB (Cosmic Microwave Background) obtained through the WMAP (Wilkinson Microwave Anisotropy Probe) and Planck missions have challenged the Cosmological Principle stating that at large scale the mass distribution of the Universe is homogeneous and isotropic. Though the WMAP and Planck data have transformed the vision of the Universe toward an heterogeneous and non-isotropic object; theoretical *sine qua non* conditions to explain the presence of large cosmic structures like galaxy clusters; at smaller scale the Universe has been always conceived as heterogeneous due to the presence of well localized material objects with radiation/radiationless emission characters. As a consequence with the Universe locally characterized by a heterogeneous and non-isotropic distribution of matter and energy, it's thermodynamical equilibrium is far to be achieved running under a non-equilibrium regime. Due to these heterogeneous non-equilibrium conditions chemistry can efficiently operate. Chemistry is classically defined as the Science dealing with the study of matter transformation, in particular with the reorganization of the atomic external electronic shells, *i.e.* valence electrons. Such a definition confines the chemistry realm within the *low energy physics* where the stronger chemical bonds are within the range of $\sim$5 eV; to mention but few representative (single) bond energies C-F = 5.08 eV, C-C = 3.60-3.69 eV, C-H = 4.25 eV and O-H = 4.77 eV; though historically the first *chemistry in space* was regarded part of nuclear physics, dealing with the nucleosynthesis of elements within the stellar core with energies on the MeV range. Adopting the *classical* definition of chemistry together with the definition of *complex molecules* when the number of atoms is > 6 [1] till recent times the chemistry of interstellar space was considered a *simple* chemistry where bi-atomic or tri-atomic molecules were synthesized. In particular the complex organic chemistry dealing with higher molecular weight molecules was addressed mainly to planets. Thanks to the development of radio-telescopes, the detection of a complex chemistry in space opened the *age of chemistry* leading to the research field of cosmochemistry/astrochemistry [2, 3]. It is not by chance that a recent review by [4] analyzing the Big bang nucleosynthesis bears the title *The Dawn of Chemistry. Primordial Chemistry and Chemical Evolution after Recombination* reports the nucleosynthesis and following classical chemistry of the first elements of the periodic table, *i.e.* ^{1}H, ^{2}D, ^{3}He, ^{4}He and ^{7}Li, elements that in addition to the CMB represent the other relics of the Big Bang [5, 6].

1.2. The Universe Chemical Evolution: Periodic Table Elements and the Transition Metals Genesis

The elements beyond the ones synthesized during the Big Bang ^{1}H, ^{3}He, ^{4}He [4] (^{6}Li, ^{9}Be, ^{10}B and ^{11}B are continuously synthesized by cosmic rays *spallation* processes [7]) are born in the stellar hot-cores or during the complex star death phenomena. Depending on their mass and metallicity stars show a characteristic evolution pattern as classically depicted by the HertzsprungâRussell temperature-luminosity diagram [8]. The first light of a star starts with the H burning phase where He is produced based on a proton-proton (pp) chain or on CNO-cycles. When the hydrogen core is exhausted and enriched in He, hydrogen burning continues in a shell embedding the same He ashes and the following gravitational contraction increases the core temperatures enough to ignite He. This phase in a star determines the *Asymptotic Giant Branch* (AGB) stage. Depending on the star mass such a process can proceed till the synthesis of ^{56}Fe in an *onion* layered structure [9], where a series of shell burnings made of ^{4}He, ^{12}C, ^{20}Ne, ^{16}O and ^{28}Si are concentrically organized around a central ^{28}Si/^{56}Fe core. The AGB stars are believed to be the main sources of carbon and nitrogen in the Universe as well as of some of the heavier nuclides [10, 11]. In particular the *Thermal Pulsating Asymptotic Giant Branch* (TP-AGB) period is characterized by a series of dredge up phenomena, allowing the star to mix the rich C, N and O deep layers up to the surface, experiencing a significant mass loss via strong stellar winds, thereby enriching the interstellar medium with the products of their nucleosynthesis [12]. Elements heavier than ^{56}Fe are to a large fraction created in the explosive nucleosynthesis such as the r-process (rapid neutron capture) [13] and rp-process (rapid proton capture) [12] while the s-process (slow neutron capture) is responsible for the nucleosynthesis in the stellar core [14, 15] with the latter bearing the fundamental role for the synthesis of about half of the elements heavier than ^{56}Fe. Specifically, explosive nucleosynthesis is characterized by p-, ν-, νp-, α- and r-processes referring to core-collapse supernovae (type II, Ib, Ic) of outstanding importance as they are predicted to be the most prolific sources of Galactic elements [16]. In fact, the explosive nucleosynthesis process is predicted to be the source of the majority of nuclides with $A > 12$. To give an idea of the amounts of the Fe group metals (first row TM) involved in a supernova explosion like SN 1987A, a total of $\sim$0.07 $M_{\odot}$ of ^{56}Co in the ejecta was calculated [17], while an estimate for the ^{56}Ni masses deduced from 17 type Ia supernovae sets a range of 0.1-1.0 $M_{\odot}$ [18]. The relative TM abundances have been estimated based on observation as well as calculated (refractory elements are not yet easily detectable) on evolutionary models of star/galaxies [19]. TM such as Fe, Co, Ni show fractional abundances of $\sim$1-10^{-2} toward Si. Higher atomic weight TM can be set with Si fractional abundances comprised between the Pb peak and the Fe peak at $1 < \mathrm{TM} < 10^{-5}$. As it will be reported in the next section all the heavy and refractory-elements are expected to be partially depleted and condensed into dust grains, resulting in an interesting concentration of active TM for a further complex chemistry.

2. Complex Chemistry in Action

Following the recent classification made by US National Research Council Astro 2010 Survey on Astronomy and Astrophysics [20] the two categories **I)** Planetary Systems and Star Formation and **II)** Stars, Stellar Evolution and Dust Grain Formation, will be considered. In such cases the fundamental chemistry/physics set by gas/gas and gas/dust grains interactions takes place with TM proposed to play an important role in the overall chemistry.

I) Planetary Systems and Star Formation. In molecular clouds a rich carbon based chemistry has been detected with the presence of molecular anions [21] and complex polycyclic aromatic hydrocarbons (PAHs), carbon chains and fullerenes as part of an extended size distribution of interstellar dust [22, 23]. In dark cold (∼10 K) interstellar clouds an unsaturated (C_nH) or bare carbon chemistry has been found [24] while in *hot cores* and *corinos*; *i.e* warm objects with temperatures of 100-300 K and associated with low mass protostars or heavy young stellar objects; a rich terrestrial like chemistry (simple alcohols, esters, ethers, nitriles) is shown. The elegant *hot cores* and *corinos* organic chemistry is probably due to the involvement of the dust surface as a catalytic site and the organic products are then desorbed or evaporated into the gas-phase [1]. In pre-stellar cores, where the stellar birth starts characterized by low temperatures ∼10 K and relatively high density during the isothermal collapse, a depletion of heavier molecules on dust particles has been suggested [25] followed by deuterium fractionation. In protoplanetary disks the detection of CO in gas-phase has been explained by photodesorption [26] and the presence of complex molecules is a function of the temperature gradient (distance from the central star and distance from the disk mid-plane). Directly linked to the proto-planetary disks, solar system comets show the composition of the primordial solar nebulae with many organic species [27]. Furthermore with a similarity between the cometary ice grains [28] and the interstellar counterpart [29], the chemical composition of the cometary one rich in H_2O, CO_2, CO, CH_3OH, hydrocarbons, nitrogen and sulfur containing compounds, minerals and silicates, sets an important window on the interstellar ice-grain chemistry where radiation processing of organic molecules on ice surfaces is suggested [30].

II) Stars, Stellar Evolution and Dust Grain Formation. After their nuclear synthesis, elements undergo a series of chemical and physical processes. In general, low-mass AGB stars are predicted to be the most prolific sources of dust in the Galaxy together with the *novae* phenomenon, frequently revealing dust forming episodes in the ejecta [31] creating a perfect condition for a gas and dust chemistry development. Close to the stellar photosphere, chemical species as well as dust condensates are formed under thermodynamic equilibrium into concentric shells centered on the mother star defined by a large temperature, density and radiation gradients [32]. As a consequence circumstellar envelopes can be well defined as *chemical factories*. For example in the C-rich shell of the AGB star IRC + 10216, have been found over 70 different chemical compounds [33, 34]. Most importantly refractory-element-bearing species (Si, P and metals) are predicted to be in some sort of mineral grain, supported by condensation models predicting that dust in circumstellar shells takes on several forms, depending on whether the environment is oxygen or carbon-rich [35]. However, based on millimeter observations, refractory elements in circumstellar environments are not all contained in dust grains. Nine Si containing molecules have been found in circumstellar shells together with eleven molecules containing metals [36]. In C-rich envelopes, metals are present as halides (NaCl, KCl, AlF and AlCl) or metal cyanides (MgCN, AlNC, MgNC, KCN and NaCN [37], while in O-rich shells, oxides and hydroxides such as AlO and AlOH dominate [38] with Al proposed to be condensed in Al_2O_3. The presence of AlO and AlOH indicates that photospheric shocks are likely disrupting grains. In C-rich shells, silicon is primarily present as SiC, while in O-rich objects in oxide condensates. Phosphorus is probably present in the form of *schreibersite*, $(Fe,Ni)_3P$, while magnesium is contained in silicon and aluminum oxides in O-rich shells and primarily as MgS in C-rich shells. Interestingly few molecules containing phosphorous have been observed in the ISM (Inter-stellar Medium). Phosphorus-containing molecules seem to be relatively abundant in circumstellar shells, underlined by the discoveries of CCP, PN, HCP, PO and, probably, PH_3 [39]. Furthermore carbonaceous dust outflows of late-type stars and silicates in envelopes of late-type stars give fundamental contributions to the dust presence in ISM. Carbonaceous dust particles are primarily formed by a combustion-like process where small carbon chains form PAHs (Polycyclic aromatics), nucleate into larger-size PAHs and, ultimately, into nanoparticles [40], while silicates are mostly found in the amorphous state [41] though some silicates in crystalline form have been observed in (post-)AGB stars and in disks around Herbig Ae/Be stars, T-Tauri stars and brown dwarfs [42]. The detection of silicate dust grains containing O, Si, Fe and Mg, as well as some Ca and Al, provides an important clue on dust chemical composition [36].

3. TM Chemistry in Dust Particles and Gas Phase: new Catalytic Pathways

The previous section reported a condensed synthesis on the origin and composition of the known inorganic as well as organic compounds mainly determined by multi-wavelength spectroscopy. However analyzing such compounds from the chemical-physical point of view, the complex chemistry that has been found in space can be further analyzed by considering a contribution from the single TM. To comprehend such statement it is mandatory to understand their chemical-physical behavior, well known due to their fundamental role in catalysis and industrial catalysis. In fact the occupied d orbitals makes TM elements and their derivatives possible important players in astrochemistry and *astrocatalysis* both in gas phase as well as in solid state. Interestingly a first pioneering proposal regarding TM involvement into catalysis in space was suggested by Goddard back in 1980-1990 [43], Prasad [44] and Bohme [45]. In space TM are detected in the gas phase within supernova remnants with an overwhelming presence of Fe^{+n}, Ni^{+n} and Co^{+n} or in star atmospheres and envelopes as FeO [46], FeCN [47]

Table 1. The TM chemical nature, type and occurrence does not consider planet chemistry but only objects as defined in Section 2. The term *dust* refers to a model of dust grain with a central solid core surrounded by ice (H_2O, CO, CH_3OH), while *inclusions* are intended as small solid fragments enclosed in the dust grain within the silicate core or covering ice.

Chemical Nature	**Type**	**Occurrence**
Pure Metals	Bulk	as Inclusions or Dust
	Clusters	as Inclusions in Gas Phase
	Naked Ions	Included in Gas Phase
Metal Compounds	Inorganic as Minerals	as Inclusions or Dust
Metal Compounds with Ligands	H/H_2, N/N_2, CO, H_2O	as Inclusions in Gas Phase
	Organo-Ligands	as Inclusions in Gas Phase

and TiO/TiO_2 [48]. However for 4d and 5d TM with cosmic fractional abundances of 10^{-2}-10^{-5} compared to Si, their line spectra resolution and assignment is difficult due to spectral complexity. As a consequence though there is little knowledge on their exact chemical/structural nature and localization once they left their mother star, it is possible to build an educated guess based on the known physical-chemical characters as depicted in Table 1.

The chemical reactions where TM are possibly actively involved can be selected by imposing constrains on the thermodynamic (exothermic reactions) as well as kinetic (low transition states, activation by UV or charged particles) levels, resulting in the chemical reaction typologies as ion-ion, ion-neutral molecule and radical. In the next lines follows a short synthesis on the possible role of each of the categories reported in Table 1.

a) Pure TM and TM Clusters. As pure, TM can exist in two different forms, as *bulk* where the number of atoms constituting the agglomerate is greater of what is defined as a *cluster*. TM clusters possess a size ranging from a few to several hundred thousand atoms, representing an intermediate stage in the transition from small molecules to solids, showing a characteristic differential reactivity and stereo/regio selectivity compared to the parent bulk TM [49]. Till now, though not directly considered for their chemical reactivity, formation kinetics of small clusters made of Si, Mg and Fe have been considered in the attempt to calculate dust formation in the early universe by SN ejecta derived from population III stars [50]. A further valid process of cluster formation can consider the *Mond* process where the reaction: $[TM(CO)_n]_m \rightarrow TM_m + CO_{m*n}]$ takes place in the gas-phase. When considering pure bulk TM, it is reasonable to hypothesize their contribution to the chemical composition of space dust. In general dust is defined to be formed by a silicate based material or following the Goldschmidt classification [51] by *litophile* elements. However a core of pure TM or alloy(s) can be constituted by *siderophile elements* [51] where, for example, pure dust-bulks of TM *siderophile* like Fe and Ni can be easily obtained by a *Mond* process. Such growth process is well different in type, scale and dimensions from the process taking place in a disk-planetary object, where the bulk iron based M-type asteroids are originated from large enough bodies able to melt and differentiate with the *siderophile elements* sinking into the core while leaving *litophile* elements in the crust [52, 53]. Finally and most importantly regarding their chemical reactivity, solid metals as well as their oxides can be activated by microwave, UV and electrons developing a C-C and C-H activation (see next paragraphs);

b) TM Naked Ions. TM naked ions have been proposed to be involved in the destruction/formation of CO [44], formation of HCO [44] and co-involved in the formation of PAH [45]. However TM naked ions are known to activate C-C and C-H bonds in gas phase acting on a substrate like CH_4 or higher saturated/insaturated hydrocarbons [54]. Huge efforts have been applied to the analysis and mechanistic understanding of such industrially and scientifically interesting reactions where different TM and some actinides at different charged states ($[TM]^{-/0/n+}$) have been reacted in the gas phase with alkanes [54]. For example Fe or Pt^+ can oxidize CH_4 obtaining a series of organic molecules like CH_3OH, CH_3CH_2OH, H_2CO and HCOOH. The interest of such compounds within the astrophysical contest can be found in their ability to perform an "*easy*" C-C and C-H bond activation when in electronically excited states, a condition that can be easily obtained in some environments, especially in a planetary systems and star formation zones [1]. Some previous ;

c) TM Oxides/Minerals or Inorganic compounds. This term defines all TM *minerals* from simple TMX_y, where X is a generally non-metal element like N,O or S to more complex compounds like *schreibersite* $(Fe,Ni)_3P$ or *kamacite* α-(Fe,Ni) found in meteorites, to mention few. Interestingly some minerals characterized by a layer structure working as simple support or matrix for the TM, for example in manganates where Ni or other TM are inter-layered, show a strong catalytic activity comparable to the same free amount of TM contained within the layers [55]. A structurally simple but extremely important subclass is constituted by TM oxides ($[TMO_y]^{+n}$) and as reported in the following Section in the solid state can react with hydrocarbons by use of microwave, UV and electrons for C-C, C-H [56] bond activation. Specifically in gas phase they can activate CH_4 leading to three different products: CH_3OH, metal hydroxides via loss of a $[CH_3]\cdot$ and formation of $[TM{=}CH_2]^+$ concomitant with H_2O as a neutral product. They can also react with higher saturated hydrocarbons, ethene and higher alkynes [57];

d) Metal-Ligand Compounds (L = H/H_2, N/N_2, CO, H_2O). Such simple and space abundant species can potentially form a classical metal-ligand (TM-L) bond with important catalytic activity in the synthesis of organic compounds. In fact the ability of many of the TM to interact with σ/pi-donor/acceptor species gives many of the resulting compounds catalytic activity. For example simple abundant molecules like CO or H_2/H produces carbonyl and hydride derivatives opening the pathway toward CO and H addition chemistry. In the past (1992) some $Fe(CO)_5N$ and $Fe(CO)_5H$ studies were performed with interesting applications in space catalysis [58, 43]. A further possible role can be their involvement as *sink compounds*. Because CO and H_2 can sublimate at extremely low temperatures, if not reacting both TM-CO and TM-H_2 can be retained within the dust grain and will at higher temperatures start addition reactions to organic substrates or a simple release of H_2 and CO will follow;

e) Metal-Organoligands. To mention few the TM-L bond with organic species like $H_2C{=}CH_2$, C_{60}, $R_1{=}\bullet{=}\bullet{=}R_2$, PAH can be well foreseen. The first organometallic compound was proposed back in the 1992 [59] where Fe and Ru were suggested to interact with coronenes molecules possibly involved in the olygomerization of acetylene molecules and responsible for TM depletion [60]. More recently (2008) theoretical calculations and experimental data on $[C_pFeC_{24}H_{12}]^+$ and $[C_p{}^*FeC_{24}H_{12}]^+$ complexes have been published [61] confirming the possible importance and interest of organometallic chemistry in space.

All the previous categories can be also *mixed*. For example mixing the d) and e) categories the resulting ML_CL_n compounds, to be found for example on the surface of carbon agglomerates, where L_C = organic and L_n = CO, H_2O, H_2, enhance the insertion possibilities of the L_n σ-type ligands into organic molecules. The TM compound categories previously listed in Table 1 and discussed can potentially strongly contribute to the gas/gas and gas/dust grain chemistry depending from the positioning, *i.e.* on the chemical-physical conditions where the dust grain is placed[1].

3.1. Model Systems: $[TM_mX_y]^{+n}$: the Case of $[FeO]^+$ and $[FeN]^+$

It is clear that the inclusion of TM chemistry within the astrochemistry field results in an *explosion* of possible chemical pathways to which TM can actively contribute. As previously reported, a first pioneering proposal considering the TM contribution to the catalysis in space can be dated back to the decade 1980-1990[43, 44, 45]. The idea, as later underlined by Rolando [58] was based on the fact that free atoms like H are important components of the interstellar medium. As a consequence, this statement together with the fact that TM can be potentially easily photoionized to cations, the reaction between TM^{+n} and the abundant H, N or CO is easy to reach under interstellar conditions. Due to the TM chemical richness and variety, even considering a simple analysis of the five categories previously analyzed would result in a cumbersome impossible task. However by an educating guess some TM compounds can be selected and by developing their chemistry it is possible to show how their contribution, even based on a single case, can be determinant. First selection rules must reasonably consider variables like: **a)** the cosmic abundances of the elements; **b)** thermodynamic (exothermic reactions) as well as kinetic (low transition states, activation by UV or charged particles, charged and radical states); **c)** structural simplicity of the systems involving some already known data derived by experimental or theoretical calculations and **d)** specific chemistry based on the development of a HCNO organic chemistry. Therefore the most abundant elements apart from H and He are (ordered by a decreasing scale) O, C, Ne, Fe, N, Si, Mg, S and are able to develop an organic HOCNS chemistry and dust inorganic chemistry. By considering molecular simplicity, reactivity and abundances, TM oxides $[TM_mO_y]^{+n}$ and TM nitrides $[TM_mN_y]^{+n}$ possess an interesting chemistry (developed in the next lines) [62, 63, 54] that can be (co)-involved in the synthesis of organic compounds in the gas phase or as inclusions within/on the surface of dust grains. However word of caution should be addressed. Though the selection rules applied are reasonable, the real amount of the TM oxides and TM nitrides produced in star envelopes or SN outbursts must be in the future better analyzed. This can be reached by introducing detailed physical and chemical kinetic variables as used, for example, in kinetic models for the condensation of carbon dust[64] or by introducing elegant non-steady-state formulations for the analysis of small clusters and grains growth (C and $MgSiO_3$) in the ejecta of supernovae [65]. From the observational point of view the TM oxides presence is confirmed by the detection of FeO, TiO/TiO_2 [48] and CrO [66] all spectroscopically assigned (though FeO has to be confirmed) while TM nitrides have been not yet assigned though SiN [67, 68] and PN [69] have been detected. Because of the reactivity, the attention can be restricted to the singly charged states of the iron oxides and nitrides like $[FeO]^{+1}$ and $[FeN]^{+1}$ (higher oxidation states would simply improve the reactivity), although (see later) the electronically excited states of the same compounds or even of the neutral form can be strongly reactive toward organic substrates. In fact in gas phase: **I)** electronically excited naked TM ions are able to dehydrogenate CH_4 [63] through a reaction sequence: $TM^+ + CH_4 \rightarrow TM(CH_2)^+ + H_2$; **II)** if thermalized only 5d naked TM ions can dehydrogenate CH_4; **III)** however thermalized ligated $[TMO_y]^{+n}$ react with CH_4, small alkanes and alkenes with a tree of products like (see Figure 1)

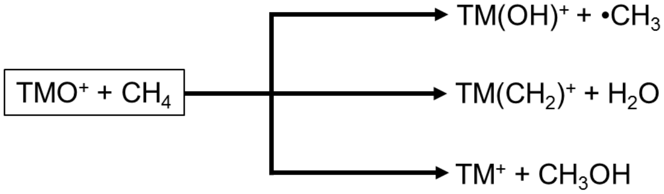

Figure 1. Tree of products of a general cationic TM oxide activating the C-H bond of CH_4

strongly dependent from the TM if a (late) 3d, or if a 4d/5d and oxidation state [70, 62]. The reaction tree in Figure 1 has been already analyzed considerably well for a series of 3d, 4d and 5d TM though only at lower oxidation states [56, 62]. However another extremely important reaction is **IV)** the nitrogen addition through the sequence

$TM(CH_2)^+$ + NH_3 →(C-N) products that can be achieved only with 5d thermalized TM. As a consequence in case of Fe, its carbene is not active toward ammonia, while its nitrido form $[FeN]^+$ (Figure 2) allows access to the amination of organic substrates, as suggested by [70].

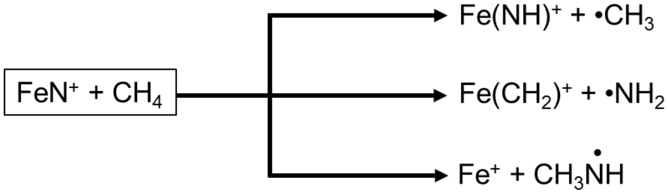

Figure 2. The nitrido-iron cation tree of products activating the C-H bond of CH_4

Nitrido-iron compounds are extremely reactive species and the few laboratory compounds ligand stabilized were isolated at extremely low temperatures after thermal or photochemical oxidative elimination of molecular nitrogen from an azide complex obtaining high Fe(IV), Fe(V), Fe(VI) oxidation states [63, 71, 72], while the most simple $[FeN]^+$ has not been produced in sufficient amount for experimental analysis [70]. Considering the astrophysical environments the presence of the $[FeN]^+$ ion in certain stars [73] have been suggested but not further confirmed, though the importance of the neutral [FeN] was addressed in an experimental work to determine the rotational constants [74]. The parental inorganic compound Fe_2N (capable of slowly reacting with water emitting NH_3 fumes) and FeN have attracted some attention due to their important technological applications (steel nitridation as well as its colloidal solutions to obtain ferrofluids) [75, 76]. Most importantly as shown in Figure 2, the iron imido-cation $Fe(NH)^+$ is known to be reactive toward O_2, H_2O, H_2, ethene, benzene, ethane, propane but not toward CH_4 [77]. It is quite curious to note that $TM(NH)^+$ is formally isolobal to $TM(CH_2)^+$ and TMO^+ and therefore the inertness toward CH_4 would need further investigations [78]. In Figure 3 a synthesis where a reaction network of both $[FeO]^+$ and $[FeN]^+$ are involved in substrate oxydation/amination is reported.

Figure 3 is strongly limited and restricted not showing the following radical product chemistry and Fe^+ ion reactions. Interestingly in the $[FeN]^+/CH_4$ (or with higher alkane) reaction, a NH_2 is released and this together with the possible photo-ionization of $Fe(NH)^+$ can help to explain the detected presence of NH and NH_2 in absorption in diffuse gas, where existing gas-phase and grain surface chemical models cannot adequately explain the data [79, 36].

In Figure 4 a possible *paper chemistry* of the reactivity of $[FeX]^+$ with X = N or O toward higher alkanes (C_2H_6, C_3H_8) and alkenes ($H_2C{=}CH_2$) is shown. To close the disquisition on the Fe oxide and nitrido compounds some further points should be underlined:

a) the reactions can perform in the gas phase as well as on/in the ice of a dust grain. The difference between the two environments will influence the number of ligands (L)

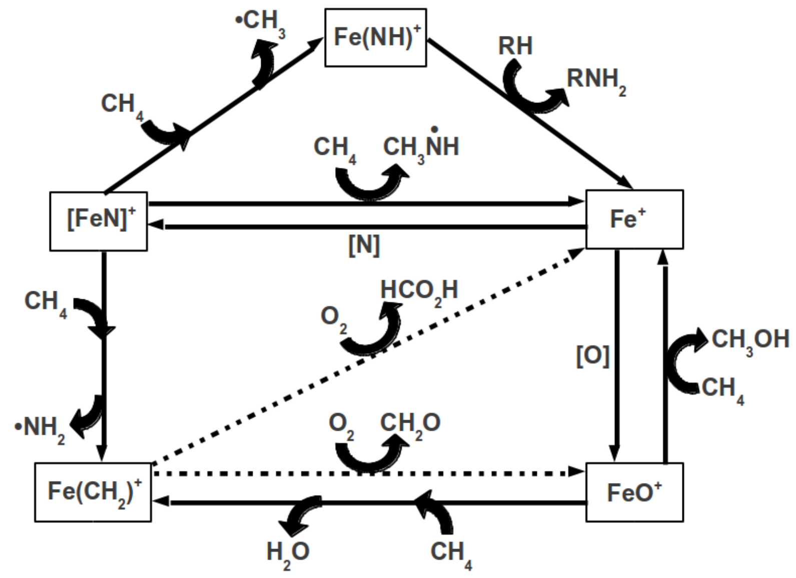

Figure 3. Network of chemical reactions connecting the oxidation and amination products of Fe oxide and nitride.

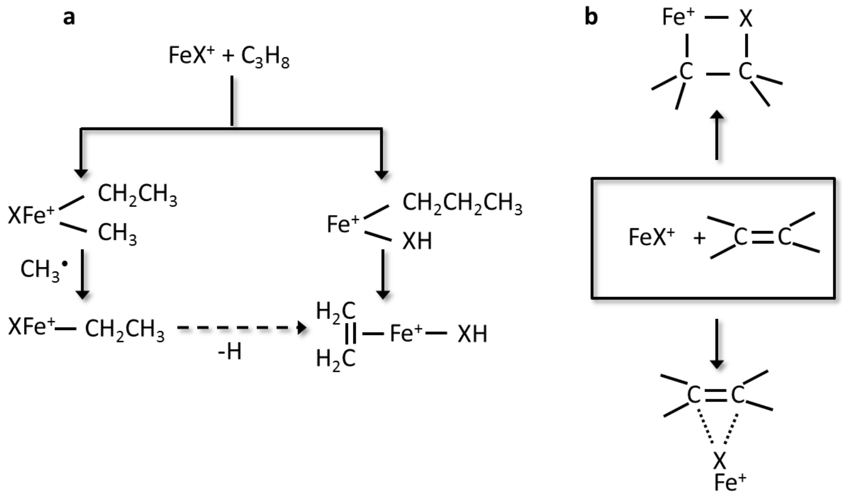

Figure 4. Some possible activation products and transition states of a general $[FeX]^{+1}$ cations. In Scheme 4b for the ethene reaction only two possible transition states are reported.

present on the iron center, especially if closed shell CO ligands are involved. In fact the L sphere will affect the *carbene* or *alkylidine* character of the $Fe(CH_2)^+$ as well as the selectivity toward the C-C or C-H as known for the M^+ or MO^+ species [70]. It is reasonable to expect the same ligand effect on $[FeN]^+$ (C-N bond selectivity);

b) both $[FeO]^+$ and $[FeN]^+$ (Figure 3) can end up in the carbene $Fe(CH_2)^+$, a *dead-end* for a first row TM like Fe. However the reactivity of such a compound toward oxygen/nitrogen can be modulated by photo-excitation to higher electronic states as well as possible photo-ionization resulting in the release of the methylidene $:CH_2$ fragment;

c) other substrates as well as ligands can be considered, where the richness of the Fe spin states involved in a catalytic scheme (Figure 3) can help the catalysis by spin-crossing; **d)** last but not least, the attention has been focused on the C-C and C-H bond activations by O and N atoms. However, another abundant possible iron compound with an interesting organic chemistry is the iron sulfide or $[FeS]^{+n}$ (the abundances have been calculated, for example, in the ejecta of SNe Ia [80] and SNe III [81, 50]) important in the possible development and formation of the organic sulfur chemistry like thiols (C_nH_{2n+1}-SH) [82]. It is clear that though there has been a limited selection of the possible TM compound chemical *dimensions*, the potential of their contribution to space chemistry is humongous.

4. Conclusions

The aim of the present study is to propose and develop the role held by transition metals (TM) and their related fine and rich chemistry within the astrochemistry background. Based on the actual known chemical characteristics and reactivities, the TM contribution can be foreseen in both gas and solid state chemistry and homogeneous/heterogeneous catalysis by developing a complex net of chemical reactions by gas/gas and gas/dust grain interactions. To distinguish their chemistry; function of their physical state, state of aggregation and chemical interactions; TM compounds have been classified in five main groups, respectively: **a)** pure *bulk* TM, **b)** TM clusters, **c)** TM naked ions, **d)** TM oxides/minerals, **e)** TM-L (L= ligand) with L $= \sigma$ and/or π-acceptor/donor species like H/H_2, N/N_2, CO and organic molecules like C_p, PAH, $R_1{=}\bullet{=}\bullet{=}R_2$. Placing TM in space, their reactivity is function of the temperature, radiation field and chemical composition and consequently, dependent from the astrophysical object in which TM are localized like interstellar medium (ISM), molecular clouds, hot cores and *corinos*. However even a simple analysis of the five aforementioned categories would lead to a cumbersome task. As a consequence some simple selection rules have been applied to choose the systems to be analyzed on the following parameters: **a)** the cosmic abundances of the elements; **b)** thermodynamic (exothermic reactions) as well as kinetic (low transition states, activation by UV or charged particles, charged and radical states); **c)** structural simplicity and **d)** specific chemistry based on the development of a HCNO organic chemistry. Following the aforementioned selection rules TM compounds showing an active HCNO chemistry are the naked TM themselves or characterized by the general formula: $[TM_mX_y]^{+n}$ with +n=total charge and X representing a second non-metallic element. Specifically TM oxides $[TM_xO_y]^{+n}$ and TM nitrides $[TM_xN_y]^{+n}$ possess an interesting chemistry [62, 63, 54] that can be (co)-involved in the synthesis of organic compounds in the gas phase or as inclusions within/on the surface of the dust grains. To limit further the working example, the focus was applied to the chemistry of the iron oxide $[FeO]^{+1}$ and the extremely reactive iron nitride $[FeN]^{+1}$, able to perform C-C and C-H bond activations resulting in a C-O and C-N compounds furthermore opening the pathway to the organic compounds oxydation/hydroxylation and nitrogenation/amination. For example both $[FeO]^{+1}$ and $[FeN]^{+1}$ can help to explain the detected presence of NH and NH_2 and CH_3OH in absorption in diffuse gas, where existing gas-phase and grain surface chemical models cannot adequately explain the data [79, 36, 1]. The simplicity of the model chemistry based only on Fe oxo and nitrido compounds suggests the enormous potential that such new chemical actors can introduce. Obviously there is still a long way to the top before the effects and contributions of TM to space chemistry are unraveled, *i.e.* between the four proposed selection rules, the real amount of $[FeO]^{+1}$ and $[FeN]^{+1}$ produced in the ejecta of supernovae or late type stars must be better developed in the near future. Furthermore many other important metals like Co, Ni and non-metallic elements like S can further introduce a real *fine* chemistry Finalizing, the preamble is promising and TM fine chemistry has a high probability to add its contribution to the known synthesis of organic compounds opening a new perspective in the astrochemistry field whose qualitative (type of compounds) and quantitative contribution must be unraveled.

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