Molecule formation in plasmas and at surfaces.

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Abstract: New molecule formation at surfaces from radicals dissociated in the plasma is a very important process in e.g. plasma conversion and plasma etching. In plasmas radical fluxes to the surface are large and surfaces are passivated with radicals, thus changing association conditions. In molecular mixtures new molecules can be generated from fragments of injected molecules. Low pressure experiments show that the surface is important. Experiments with different plasmas and different surface materials show that a pattern exists: In H/C/O seeded plasmas predominantly CO and H\textsubscript{2} are formed, with other molecules in smaller quantities. If N is present also HCN, NO and NH\textsubscript{3} (if O poor) are formed. The results prove quite similar for totally different plasmas and surfaces, indicating a more chemical formation process at the surface.

\textit{Keywords:} molecule formation, surface processes, dissociation, plasma

1. Introduction

In several branches of plasma chemistry the formation of new molecules from radicals in plasma and at the surface is an important process. It is essential in plasma etching as material is removed in the form of volatile molecules; etching was a first example of the importance of surface processes in molecular plasmas. For the re-generation of homonuclear molecules as H\textsubscript{2}, N\textsubscript{2} or O\textsubscript{2} after dissociation in the plasma, surface processes are key processes. This collaborative work is aimed at the study of molecule formation in H O N and C containing mixtures, with emphasis on non-depositing plasmas. Understanding of the (underestimated) importance of surface processes for the plasma chemistry is one of the key subjects of this work.

In experiments \cite{1} in hydrogen with an expanding plasma fed by a thermal plasma source delivering H atoms, still hydrogen molecules proved to be the main neutral present despite the efficient atomization in the thermal source. The reason is that H atoms re-associate at surfaces in times $\tau_{\text{H}}$ short compared to the residence time, $\tau_{\text{res}}$, even though the probability of H\textsubscript{2} formation at the surface is 0.1. The lifetime of the atom is thus short compared to the residence time and thus H/H\textsubscript{2} ratio is $<<$ 1 even if the source delivers only atoms. These processes become clearer in the ETP approach, with a thermal source delivering ionized atomic plasma and an expansion in low pressure chamber. The downstream plasma is recombining with low $T_e$ and thus dissociation is determined by charge transfer and dissociative recombination.

The presence of the H\textsubscript{2} molecules has a large impact on the plasma \cite{1}: it causes the anomalous electron/ion recombination in H containing plasmas (called MAR in fusion research) initiated by H\textsubscript{2} in from the surface. Thus surface processes influence plasma chemistry. But also the plasma influences surface processes: the flux of H atoms to the surface is large and in a time $\tau_{\text{cov}}$ ($\approx$ msec), short compared to the residence time ($\tau_{\text{res}}$ ~sec) the stainless steel surfaces become saturated with H atoms. Then the surface chemistry is passivated and thus the surface processes altered by the plasma.

In a nice experiment \cite{2} this process of wall loading was demonstrated for oxygen in a helicon plasma at 53 Pa. The pulse duration of the power (100W) was varied from very short times (too short to produce one monolayer O atoms) to long times (more than sufficient to cover the surfaces of the metallic reactor). The oxygen atom density profile and time decay were measured with Tali\textit{f} and the effective coefficient of association, $\gamma$ determined. It proved that for short pulse and thus bare surfaces $\gamma$ was close to 1: i.e. each arriving O atom was bound at the surface and thus lost from the gas phase. For longer pulses (thus full coverage) the $\gamma$ was around 0.1 and the time constant became longer. This is a sign of reflection of O atoms at O saturated surfaces. This was also visible in the profile of O atoms: it developed from a diffusion type profile to a flat
profile caused by reflection at the surface. Thus the surface is altered and the altered surface changes also the plasma chemistry as O atoms reside longer in the plasma.

It is generally accepted that in pure homo-nuclear plasmas (H\textsubscript{2}, N\textsubscript{2} or O\textsubscript{2}) molecules are formed at surfaces for low enough pressure (no 3 particle association). However, for mixtures of even homo-nuclear gases this is not a priori clear as now in some cases 2 particle reactions may also lead to new molecules. However, broadly speaking it is still so that 3 particle reactions are absent and 2 particle reactions nearly always yield also new radicals; the produced radicals will remain radicals in reactions even if they are altered. Thus even if a plasma path is possible (as for NO) then still the surface association is important as well, as was illustrated in the work by van Helden [3] and Zijlmans [4].

In this work the essential information has primarily been obtained from the depletion of injected and the generation of new molecules, as these gives direct information on the conversion processes. It should be mentioned that other information can be obtained from measurement of radicals. In mixtures many radicals may be active and additional information could be obtained by measuring these, as has been done for e.g. CH, OH and NH\textsubscript{x}. [5, 6, 7]

The notion of saturated surface means also that the chemical nature of the surface becomes screened off by absorbed atoms and that surface processes are changed [8]. To study this a detailed inter-laboratory study was undertaken to compare formation of molecules in several mixtures. Two different plasmas were used to compare the production of molecules: an expanding thermal plasma in argon, with molecules seeded in the expansion vessel (TU/e) and a planar microwave plasma (INP). In the experiments reported here the flows of molecules were chosen such, that in both experiments most injected molecules could be dissociated at least once in the residence time. Thus most molecules will undergo the dissociation/association cycle. For the ETP plasma this meant that the flows of injected gases were of the same order as the ion flow from the source [9]: 300 sccm. The planar microwave plasma is operated mainly on argon with only around 1% injected gases [10].

**Experiments in expanding plasma and planar microwave plasma with H/N/O admixture**

Several mixtures have been investigated with the expanding thermal plasma in Ar. One of the first was the conversion of N\textsubscript{2} and H\textsubscript{2} in NH\textsubscript{3} at a pressure of 20 Pa [11]. At roughly the ratio of 1/3 for N/H the conversion to NH\textsubscript{3} was maximal (12% of admitted N\textsubscript{2} and H\textsubscript{2}). This is a large fraction in view of the competing N\textsubscript{2} and H\textsubscript{2} re-formation. At low N admixture (near full H\textsubscript{2}) the injected nitrogen came fully back as NH\textsubscript{3}, pointing to addition of H atoms at the surface (N\textsuperscript{s} $\rightarrow$ NH\textsuperscript{s} $\rightarrow$ NH\textsubscript{2}s $\rightarrow$ NH\textsubscript{3}).

In both the ETP plasma as the planar microwave discharge the formation of NO (and NO\textsubscript{2} and N\textsubscript{2}O) was measured [12]. The conversion of dissociated N\textsubscript{2}/O\textsubscript{2} into NO proved to show the same behavior in both plasmas, including the small effect which H\textsubscript{2} has on the NO formation. In fig 1 these first results are shown for NO formation in the microwave plasma, measured with laser diode absorption.

![Figure 1. NO formation in INP planar microwave reactor; NO densities are expressed as % of injected N\textsubscript{2} + O\textsubscript{2}.](image)

The formation of NO, NO\textsubscript{2} and N\textsubscript{2}O has also been studied extensively in the ETP plasma [9]. Here we focus on results for conditions, when small amounts of N\textsubscript{2} and O\textsubscript{2} were injected (measured with mass spectrometry). Results are shown in fig 2.

It proved from Chemkin modeling [9] that the NO formation was for an appreciable part due to surface processes though also the N induced dissociation of O\textsubscript{2} is important at the higher gas temperature in the ETP plasma. Note though, that the formed O atoms
still associate to O\textsubscript{2} at the surface. The formation of N\textsubscript{2}O and of NO\textsubscript{2} can only be explained by surface processes (also for NO for low N admixture). For NO seeded plasma [13] it proved that, if dissociated, the result was very similar to the N\textsubscript{2} O\textsubscript{2} injection case: mainly N\textsubscript{2} and O\textsubscript{2} and a few % NO. Dissociation in the plasma and association processes (also) at the surface can thus change the gas composition which may thus differ from that of injected gases.

![Graph](image)

**Figure 2.** NOx formation in ETP expanding plasma reactor; NOx densities are expressed as % of injected N\textsubscript{2} + O\textsubscript{2}.

Molecule formation at surfaces is thus a dominant process as was also demonstrated in pulsed experiments in Eindhoven [4] and in the Ecole Polytechnique [14].

When hydrogen was added to the N/O additions not much change was observed. This is in contrast with the addition of oxygen to the N/H injected case: then the formation of NH\textsubscript{3} was severely impeded with even small amounts of oxygen and instead H\textsubscript{2}O was formed with ~10% efficiency [9]. With small O admixture most of the oxygen ended in water and not in O\textsubscript{2}. These results point to an important role of OH also at the surface.

These experiments in H/N/O mixtures were also performed in the microwave planar plasma in INP Greifswald [10]. Care was taken, that also here the injected gases in the argon plasma could be dissociated to a large extend, like in the ETP plasma. These experiments were carried out at 1.5 mbar and 1 kW power. The total ion production is estimated to be 1-2 \(10^{19}\) s\(^{-1}\) and thus a flow of 30 – 60 sccm molecular gases can be dissociated during the residence time.

The results were very similar: Again mainly the gases N\textsubscript{2}, O\textsubscript{2} and H\textsubscript{2} were reformed; NO was formed at a maximum of a few % in N/O, and remained if hydrogen was added, NH\textsubscript{3} was formed in N/H mixtures, but disappeared if oxygen was added to the mixture and H\textsubscript{2}O was formed instead. The plasma is different, the surfaces are different (aluminum and quartz versus stainless steel) and still similar fractions of produced molecules point to a more chemical governance rather than fully kinetic one. The results suggest that the formation or presence of radical groups as NH\textsubscript{2}, OH, NO at the surface is essential for molecules to be formed. The composition of the adsorbed layer at the saturated surface thus changes with change of injected gases leading to new molecules formed.

**Experiments in expanding plasma and planar microwave plasma with C/H/O/N admixture.**

When carbon is added to O/H mixtures, deposition becomes possible if C>O. This complicates the analysis as now C and H in (new) molecules do not need any more to add up to C and H in the injected flows as in non-depositing mixtures. With O>C deposition is absent (and even etching of remaining carbon occurs). The main outcome is that CO (and H\textsubscript{2}) is formed predominantly from radicals formed in the plasma [9,10, 8]. A possible formation route of CO and H\textsubscript{2} could be formation of HCO\textsuperscript{+} at the surface which associates with H to H\textsubscript{2} and CO\textsubscript{2}, which both desorb. This result of CO and H\textsubscript{2} formation from plasma dissociated radicals appears to be rather general. It has earlier been observed in CH\textsubscript{4}/O\textsubscript{2} plasmas with added H\textsubscript{2} [15]. In these experiments also CH\textsubscript{3}OH and CH\textsubscript{2}O were observed. In particular the methanol formation is interesting: if 3p reactions are absent, it can only be produced at the surface. Recently [16] this was also concluded in astro-chemistry. In the very dilute, hydrogen rich astrophysical plasmas also small organic molecules as methanol are observed, which are now thought to be produced at the surface of clusters.
Earlier work in Greifswald [17] and in Cambridge [18] had already shown the production of small organic molecules in CH$_4$/O$_2$/N$_2$/H$_2$ plasmas. In these cases the dissociation was far from complete as can be observed from the small depletion of CH$_4$ and from the generated CO. It is likely that larger molecules formed at the surface benefit from a small ionization degree and thus partial dissociation as then they can survive better the plasma dissociation.

In C/H (N) mixtures (without oxygen) the injected hydrocarbons are effectively depleted if dissociation is sufficient and deposition and cluster formation takes place. A view of this process gives the H$_2$ generated, which contains the part of the hydrogen from the depleted monomer. This has been observed e.g. in a nice experiment of the Fukuoka group [19]; they used Raman scattering to measure relevant molecular densities as function of flow (thus residence time). At low flows full dissociation and depletion of the injected CH$_4$ is approached with some conversion to C$_2$H$_6$ and C$_2$H$_2$, with densities much smaller than injected CH$_4$.

When nitrogen is added the main difference is the generation of HCN and NH$_3$ [15]. Dissociated N comes back mainly as N$_2$ except for small N admixture. HCN is generated in an appreciable fraction, which is also interesting from astro-chemistry perspective.

Conclusions

This comparison study of molecule plasmas in two very different experiments has shown strong similarities in the patterns of molecule formation. In N/O mixtures the main products are N$_2$ and O$_2$ with NO and NO$_2$ and N$_2$O in smaller fractions. In N/H mixtures it proved that NH$_3$ is produced in significant fraction in particular for hydrogen rich mixtures. If O is added to this mixture then NH$_3$ is strongly decreased and H$_2$O is formed. In C/H/O mixtures the main products are CO and H$_2$ (if O< 2C) whereas for O> 2C, CO$_2$ and H$_2$O are important products. For these results the composition of injected gases proved to be not of great importance: if the gases are dissociated, the end result because of conversion is relatively independent of feed gases.

It is argued that the surface must play a dominant role in the production of the molecules from the plasma dissociated radicals. For that reason the molecule formation remains similar for even very low partial pressures of injected and produced molecules down the (sub) Pascal range. A possible mechanism is the formation of molecules at passivated surfaces in an activated process. Then, at low partial pressure of molecular feeds and not too strong excitation, surface produced complex molecules as methanol can survive the plasma dissociation and be observed, thus giving evidence of surface processes.

Acknowledgement

The continuous support from the Leibniz Institute in Greifswald and the group PMP of the TU/e for this collaborative effort is gratefully acknowledged.

References