Crossed-beams and theoretical study of the reaction dynamics of O(3P) with cyanoacetylene and acrylonitrile

Introduction:

Nitrogen oxides (NOx) represent a concrete risk to human health and have become a matter of concern for their environmental effects, such as acid rain, photocatalytic smog, and the accumulation of ground-level ozone. In order to rationalize the total concentration of NOx in the atmosphere, predict their evolution, and limit their emission, combustion is one of the most important processes that should be taken into account. In addition to natural and biogenic sources, in fact, coal and coal-derived bioanalts contain organic nitrogen and pyridine and pyridine functional groups: their thermal decomposition generates many nitrogen-based compounds that can undergo subsequent oxidation to NOx. To fully understand these processes, accurate and detailed combustion models are needed, where all elementary chemical steps, their primary products, and channel specific rate constants as a function of temperature and pressure are included. In this context, we have investigated the dynamics of two important elementary reactions: O(3P) + CHCCN (CHCN and (CH)2CN) in fact, although it has been assumed in some models that the main precursors of NOx are HCN and N2H, the pyrolysis of both heterocyclic compounds, such as pyridine, pyrimidine, 2-picoline (the nitrogen analogue of toluene), and pyridine, and others, such as acrylonitrile, is characterized by a distribution of products, including CHCN and CHCN/CH.

The cross-molecular beam (CMB) technique (see Table 1) allows for the investigation of high-energy collisions to be carried out in a multichannel and multiproduct mode, and the role of intermolecular mixing (ISC) in the experimental results, which are always discussed in the light of dedicated electronic structure calculations of the underlying triplet and singlet potential energy surfaces (PES) and the comparison between the experimental BFs and the theoretical estimates of the relative yields. The CMB technique will permit to validate the PES in such a way that accurate and reliable parameters for improved combustion models can be derived.

Theory:

Regarding the PESs, the geometries of the stationary points were optimized using density functional theory (DFT), with the B3-3 parameter exchange and Lee-Yang-Parr correlation functional (B3-BS5P), the energies of the optimized geometries were computed at coupled-cluster level, including single and double excitations and a perturbative estimate of connected triples (CCSD(T)). Both methods were used in conjunction with the correlation consistent valence polarized basis set aug-cc-pVTZ.

**The O(3P) + CHCCN reaction**

**Product angular and translational distributions**

Formation of CHCN + N and CHCN/CHCN + CO from the O(3P) reaction. In particular, the reaction 

\[
\text{O(3P) + CHCHCN} \rightarrow \text{HCCN} + \text{CO} + \text{N}
\]

\[
\text{O(3P) + CHCHCN} \rightarrow \text{CHCN} + \text{C} + \text{N}
\]

**Reaction Energy Distribution**

The reaction energy distribution is shown in Figure 3. The reaction has a negative reaction energy, as expected for an exothermic reaction. The most probable reaction energy is approximately -100 kcal/mol, which is consistent with the experimental findings.

**Theoretical Estimates**

The theoretical estimates of the relative yields are shown in Figure 4. The yields are calculated using the coupled-cluster method (CCSD). The theoretical estimates are in good agreement with the experimental results, with a slight overestimation of the CHCN yield.

**Conclusions**

This work shows that the combination of crossed molecular beam experiments and theoretical calculations allows us to understand and interpret the reaction dynamics at the molecular level. In particular, on the basis of our experimental results, we found that the O(3P) + CHCCN reaction leads to the formation of CHCN + N and CHCN/CHCN + CO. The reaction energy distribution is shown in Figure 3. The reaction has a negative reaction energy, as expected for an exothermic reaction. The most probable reaction energy is approximately -100 kcal/mol, which is consistent with the experimental findings. The theoretical estimates of the relative yields are shown in Figure 4. The yields are calculated using the coupled-cluster method (CCSD). The theoretical estimates are in good agreement with the experimental results, with a slight overestimation of the CHCN yield.