

MODELING THE DESORPTION OF NO_x SPECIES IN THE COMBUSTION OF COAL

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Introduction

The mechanism at the molecular level of the evolution of nitrogen species from the char surface is not known for certain. In particular, the formation mechanism of N₂O, HCN and HCNO in the combustion process is of a particular interest in the scientific literature due to its effect in the global warming and in stratospheric ozone depletion. The mechanism of the N₂O formation during char combustion has been proposed to occur through different paths. First, by a heterogeneous reaction between the nitrogen contained in the char with the NO molecule in the presence of oxygen. Second, by a homogeneous reaction between HCN released from the char surface with molecular oxygen. Both reactions are supported by experimental measurements. An extended review concerning N₂O evolution from heterogeneous and homogeneous mechanisms can be found in the literature.¹

Due to experimental difficulties determining the fate of nitrogen containing char, resolution of the various hypotheses on the evolution of nitrogen species has been difficult. Thus, molecular orbital calculations can be an alternative tool for studying the mechanism of nitrogen release in the combustion of coal. Schematic energy profiles of the different possible channels for desorption of N₂O molecule from char-containing nitrogen species can be a reference point for a detailed mechanism of the desorption process of nitrogen species. The present study focuses on the heterogeneous mechanism and examines the evolutions of N₂O from the heterogeneous reaction between NO molecules and carbon-nitrogen systems in the presence of oxygen.

Computational details

Theoretical model. We have used the hybrid B3LYP DFT functional level of theory using the 6-31G(d) basis set to calculate energies and geometries of the models. Unrestricted Open-Shell wave function was used in all open-shell cases because the spin contamination is reasonably small.² All calculations were done using Gaussian 98.³

Physical model. The reaction of a single NO molecule with char-nitrogen bound was carried out using carbon models shown in the Figure 1. Model z4/p contains a pyridine group and represents the reaction of NO in the absence of nitrogen. Model z4/pe differ from the z4/p model in that it contains a preadsorbed oxygen atom to represents the reaction in the presence of oxygen. Pyridine group was selected because it is one of the most abundant nitrogen species in a carbonized material obtained from coal. Epoxy oxygen group was used because it has the ability to decrease the strength of the closest carbon bonds. Although, epoxy oxygen group has no been identified experimentally in char surfaces, it has been proposed by molecular orbital theories⁴ and it is used in this study. The models selected are a small subset of nitrogen and oxygen groups presented

during the combustion of coal. A more complete set of models is presented in a forthcoming full paper. Figure 1 also shows the two adsorptions directions of the NO molecule to the carbon model, side-on and N-down adsorption. In all cases, the interaction N-N was selected in order to study the desorption of N₂O in a subsequent step of the reaction.

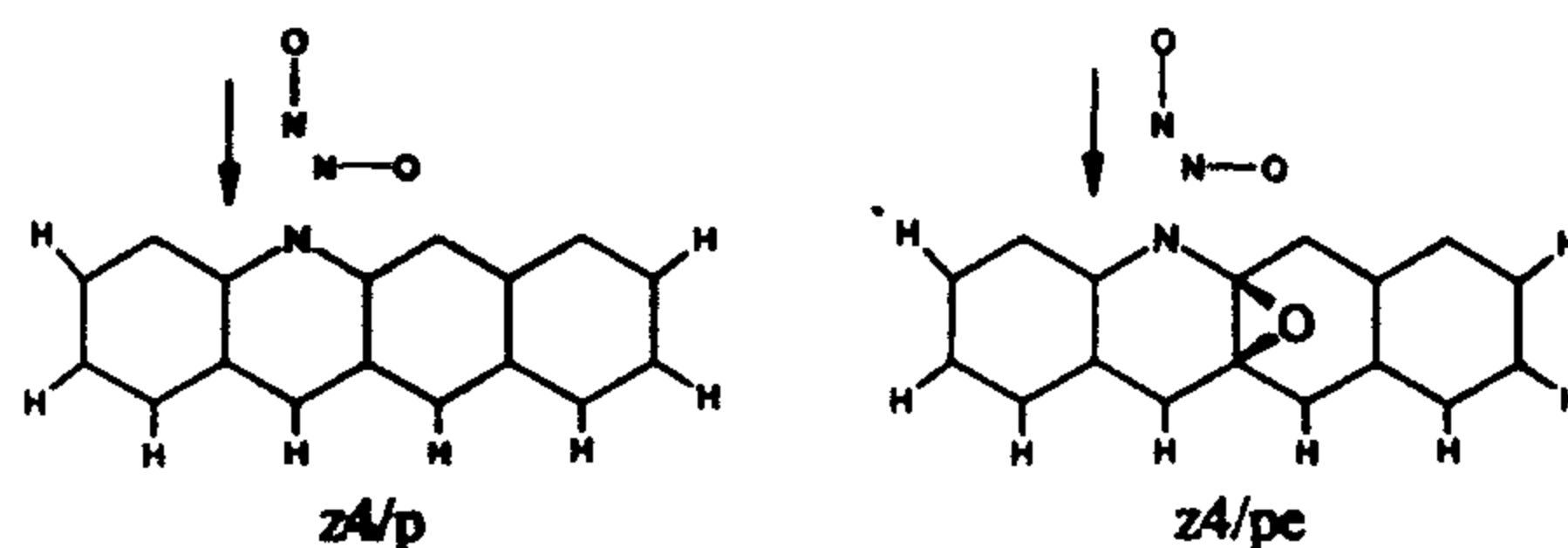


Figure 1. Model of nitrogen containing char. z4: zigzag four rings. p: pyridine, e: epoxy.

Results and discussion

Reaction of NO with char-nitrogen bound. The two models selected can give insight into the oxygen effect on the NO adsorption on Char-N bound. The system, NO molecule plus carbon model was fully optimized and stable nitrogen oxygen complexes were identified. It was found, in the char-N models selected, that the nitrogen complexes formed in the absence and presence of preadsorbed oxygen group are the same. A schematic representation of the most important part of the nitrogen group is presented in Figure 2.

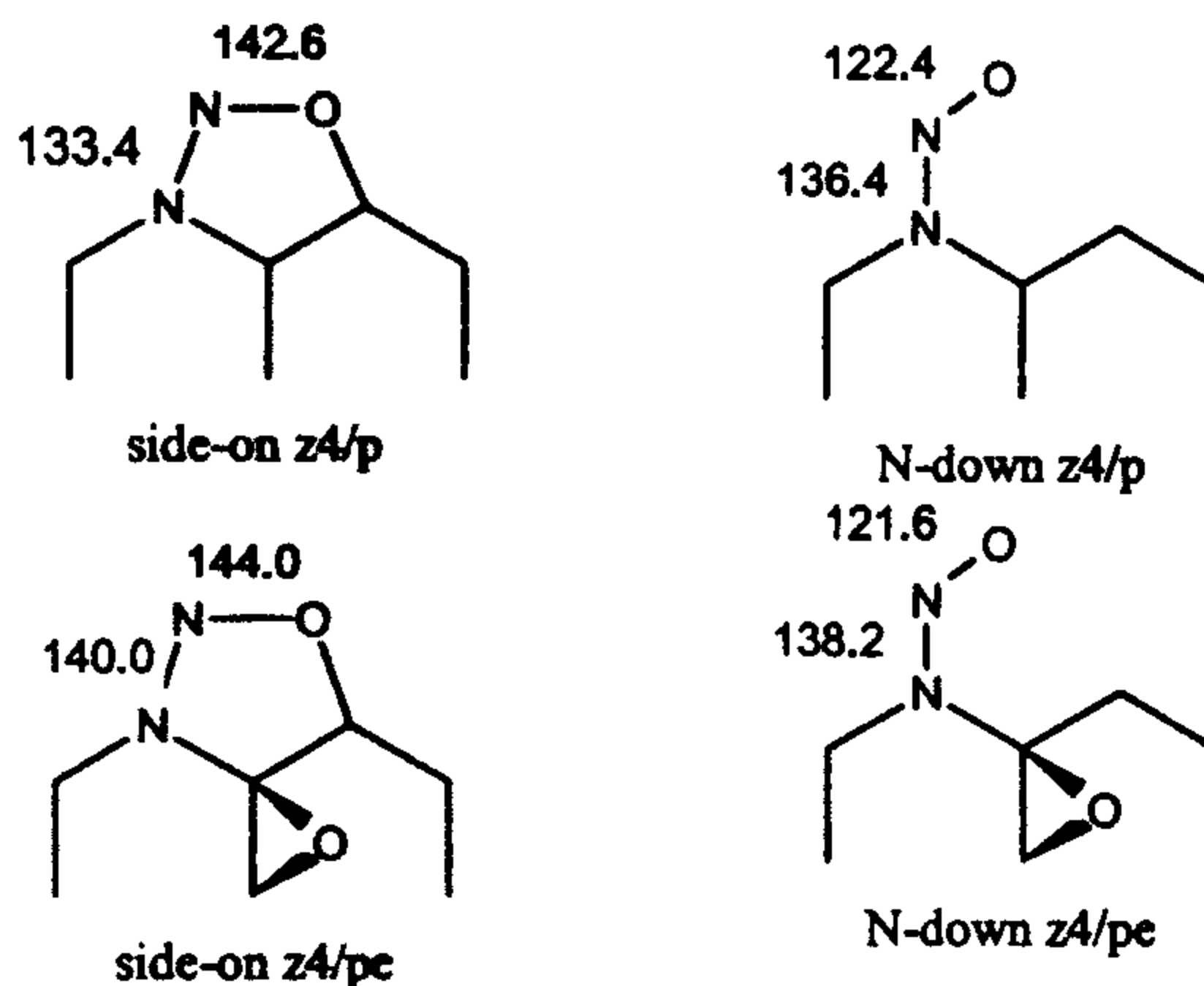


Figure 2. Nitrogen surface complexes formed by the adsorption of a single NO molecule with char-N bound models. Numbers are optimized bond lengths in pm.

The five-member ring complex (left side) is formed by the side-on adsorption and the vertical NO complex (right side) is formed by the N-down adsorption. The most important geometrical parameters of the nitrogen complexes are shown in the same figure. As can be seen, the epoxy oxygen increases the bond length of the nitrogen group in almost all cases. Although a bond length is not directly related with the bond strength, we can give a priory justification that the epoxy group decreases the stability of the closest bonds.

Adsorption energy. Table 1 shows the adsorption energy of the NO molecule on the z4/p and z4/pe char-N models. The NO adsorption energy was determined from the absolute energy of the reagents and products. It was found that the NO adsorption is an exothermic process in all cases. Adsorption of NO in side-on orientation is preferred compared to the N-down adsorption. Notice that the preadsorbed oxygen atom decreases the side-on adsorption by 28.0 kcal/mol and increase the N-down adsorption energy by 1.6 kcal/mol.

Table 1. Adsorption energy (kcal/mol) of a single NO molecule on Char-N models

Model	Adsorption energy
Side-on z4/p	-48.0
Side-on z4/pe	-20.0
N-down z4/p	-3.0
N-down z4/pe	-4.6

As the NO adsorption complexes are formed without an energy barrier, they can be formed easily in the combustion of char. Thus, different paths of N₂O desorption from these models can be analyzed. For the side-on nitrogen complex on the z4/p model, there are two channels of reaction. First, to breakdown the N-O bond and then, desorbs a N₂ molecule to the gas phase. This channel of reaction was presented in our previous report⁵ and it is not analyzed here. Second, to desorb a N₂O molecule to the gas phase by breaking the two C-N bonds and the C-O bond, as it is shown in the figure 3, -a. For the side-on complex in the z4/pe model, an oxygen migration from the epoxy group to form a six-member ring can occur, Fig 3, -c.

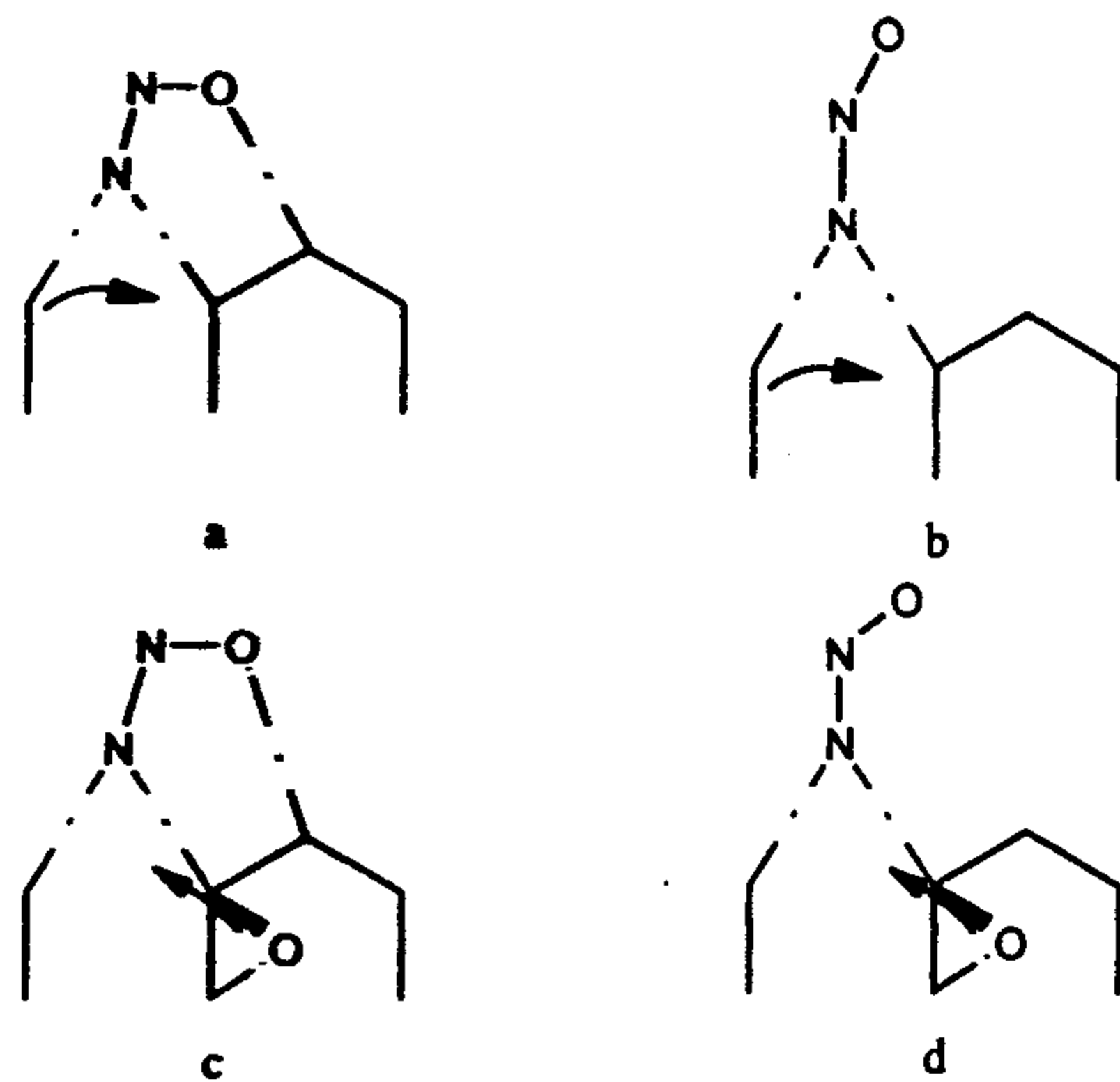


Figure 3. Possible channels for the desorption of the N₂O molecule from NO/char-N models.

For the N-down nitrogen complexes, the N₂O desorption can go through the formation of a five member ring by breaking two C-N bonds, as it is shown in the Figure 3, -b. For the preadsorbed oxygen model, the N₂O desorption can go through an oxygen migration from the epoxy oxygen group to form a six-member ring as it is shown in Figure 3, -d.

A schematic energy profile for the N₂O evolution is shown in the Figure 4. The reaction profile is obtained optimizing reagents, nitrogen complexes and products of reaction. Thus, transition states are not identified and the energy profile should be considered just as a thermodynamic probability of the reaction. As can be seen, formation of N₂O by an oxygen migration is the dominant path of the reaction. It is clear that epoxy group can increase the exothermicity of the reaction and thus, the probability of the N₂O evolution. Notice that the evolution of N₂O molecule from the side-on z4/p model implies a high-energy barrier. Hence, the evolution of N₂O in the absence of oxygen is thermodynamically not favorable. Although, we have not considered the evolution of N₂ from the NO complexes, the energy profile shows that the evolution of N₂O by the heterogeneous reaction of the NO molecule with char-N bound in the presence of oxygen is a possible channel of reaction. It should be noticed that only the epoxy group is used as oxygen source. Thus, other types of oxygen complexes should be analyzed in order to have a more complete pathways for the N₂O evolution.

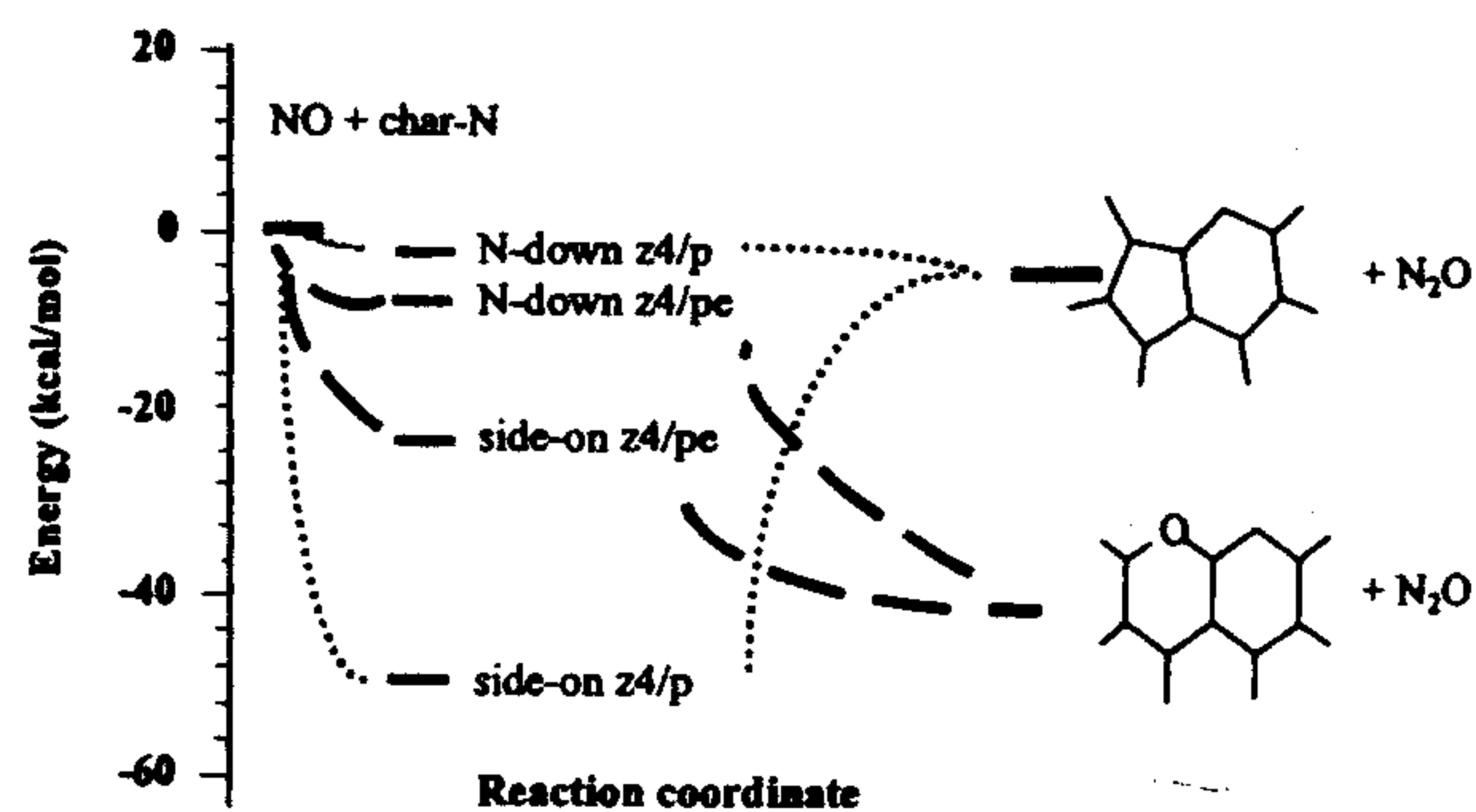


Figure 4. Schematic energy profiles of different pathways for the N₂O from NO/Char-N complexes. Energy calculations are relative to the reactants.

Conclusions

Reaction of an NO molecule with char-nitrogen in the presence of chemisorbed oxygen can release N₂O molecule to the gas phase. Oxygen migration plays an important role in enhancing the N₂O evolution. Additional calculations are being carried out on different nitrogen models, oxygen groups and for different pathways to N₂ and N₂O, particularly those involving sequential heterogeneous and homogeneous reactions.

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