INTRODUCTION

Nucleation on ions is an important process in the atmosphere. Even though the majority of atmospheric nucleation is believed to happen via neutral pathways (Kulmala et al., 2007; Mirme et al., 2010), ion induced nucleation may play some part especially in regions where air ion or ion cluster concentrations are relatively high. Ions of opposite sign were observed to exhibit different nucleation rates as early as 1897 (Wilson, 1897) but the reason for this sign preference remained a mystery for more than a century. In a recent paper by Nadykto et al. (2006) it was demonstrated that the sign effect can be predicted by carrying out relatively simple quantum chemical calculations. This means we can use quantum chemical methods to help us understand the role of ion-induced nucleation in atmospheric nucleation reactions. Recently done calculations for sulphuric acid by Kurtén et al. (2009) are just one example of the potential quantum chemical methods present. However, the computational methods in use today are generally iterative methods that employ a variety of approximations in order to keep the cost in computational resources reasonable. Because of this, theoretical predictions need to be compared with high quality experimental results whenever possible in order to gain reliable insight on the initial steps of ion-induced nucleation.

We studied the sign preference between small tungsten oxide molecules of three different species (WO₂, WO₃ and W₃O₉) and a single n-propanol molecule. The motivation for our study was an experimental study performed by Winkler et al. (2008), where a negative sign preference was observed for tungsten oxide seed particles. Tungsten oxide particle generators can be used to produce particles smaller than 2 nm in diameter. Nanoparticles such as these are valuable when studying the initial steps of nucleation and so, while the atmospheric relevance of tungsten oxide particles can be questioned, they still have an important role to play in atmospheric sciences.

METHODS

A quantum chemical study of the structure and electronic energies of WO, WO⁺, WO₂, WO₂⁺, WO₃, WO₃⁺, W₃O₈, W₃O₉⁺, (WO₂)(C₃H₈O), (WO₂⁺)(C₃H₈O), (WO₃)(C₃H₈O), (WO₃⁺)(C₃H₈O), (W₃O₈)(C₃H₈O), (W₃O₉⁺)(C₃H₈O) and (W₃O₉⁺)(C₃H₈O) was performed using the Spartan (Wavefunction Inc., 2006), Gaussian 03 (Frisch et al., 2004), SIESTA (Soler et al., 2002) and ADF (G. te Velde et al., 2001; C. Fonseca Guerra et al., 1998), quantum chemistry programs.

Tungsten atoms are relatively large, so out of computational considerations we began our studies by considering very small, neutral and singly charged seed molecules (WO₂, WO₃ and W₃O₈) and a single n-propanol molecule. This choice was also supported by the facts that the experimentally observed sign effect was stronger for smaller seed particles. For comparison with results obtained by other groups we also studied the geometries of WO and WO⁺.

In essence the work was performed in two phases. In the first phase initial guesses were both made by hand using the ADF-GUI (Wavefunction Inc., 2006) and Spartan program suites and obtained from low level (molecular mechanics) optimizations performed on some of these hand made geometries. The
geometries were then optimized with the Siesta program using the semiempirical BLYP and nonempirical RPBE density functionals in the general gradient approximation (GGA) with a DZP basis set and relativistic norm-conserving pseudopotentials for the atoms. Calculations for the neutrally charged systems were performed with spin polarization turned both on and off to probe the effect of spin polarization for closed shell systems with transition metal atoms. For the charged systems spin polarization was always turned on. Energies were taken both from the final results of the optimization runs and separate single point calculations for the geometries optimized with Siesta. The single point calculations were performed with the Gaussian 03 program suite using a meta-GGA density functional, TPSS, and a hybrid density functional, PBE1PBE, with an SDD basis set. The TPSS exchange and correlation functionals and SDD basis set were also used for re-optimization runs using the minimum energy geometries obtained with the RPBE/DZP method as initial guesses. The energies for these structures were taken from the optimization output. Finally, electronic binding energies were calculated for the systems with n-propanol and tungsten oxide by subtracting the electronic energies of the single molecules from the electronic energy of the corresponding cluster [e.g., $E_{\text{elec}}(\text{WO}_2\text{(C}_3\text{H}_8\text{O})) - E_{\text{elec}}(\text{WO}_2) - E_{\text{elec}}(\text{C}_3\text{H}_8\text{O})]$.

In the second a new set of Siesta RPBE/DZP optimizations was performed, where a total of 8 different initial geometries were obtained using the ADF molecule builder for all charging states of WO$_2$ and WO$_3$ and a total of 5 different initial geometries for all charging states of W$_3$O$_9$. Binding energies for all cases were calculated in the same fashion as in the first phase using the energies taken from the optimization runs.

CONCLUSIONS

Our results for the tungsten oxide molecular geometries showed good agreement with results obtained previously by other groups. Our results also imply a positive sign preference for tungsten oxide species WO$_2$, WO$_3$, and W$_3$O$_9$. The sign preference observed in the experiment by Winkler et al. was negative. Although there are several technical possible sources for this discrepancy, direct comparison between experiment and simulations tells us little in this case. This is due to the fact that the exact chemical composition of the seed particles in the experiment was not the focus of the experimental study and is thus not known exactly. Some of our simulation results suggest that chemical reactions may also take place, which may also alter the sign preference. However, our study was not focused on chemical reactions involving tungsten oxide other than the binding of n-propanol to the tungsten oxide seed particle.

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