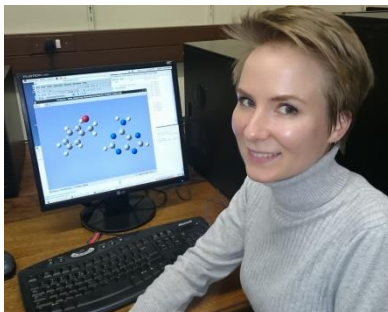


Department of Chemistry
Departmental Seminar:
Physical chemistry

You are cordially invited to a lecture presented by



Dr Dominique Buyens

Supervised by Prof Lynne Pilcher, Prof Emil Roduner and Prof Ignacy Cukrowski
Department of Chemistry, University of Pretoria

Date: Friday, 25 March 2022
Time: 10:30 – 11:20
Venue: Orbital
Enquiries: Dr. Dominique Buyens, dominiquebuyens@gmail.com

The chemical reactivity of the adeninate anion

The anionic forms of nucleic acids are potentially involved in mutations, replication and translational errors, provide scaffolds for metal organic frameworks, and are often the starting point for the synthesis of biologically active N-alkylated nucleobase derivatives. However, research into the chemical behaviour of deprotonated nucleobases is limited. In our research the complexation of the adeninate anion with sodium and potassium ions and the self-aggregation and alkylation thereof in DMSO solution was studied. Through experimental and theoretical studies, it is proposed that the adeninate anion forms ion-pairs with Na^+ and K^+ ions in which the two counter ions most likely coordinate in a bidentate and/or unidentate fashion at the N3 and N9 nitrogen atoms of the purine ring. The binding of Na^+ is preferred over K^+ , having the Na^+ result in highly favourable charge polarization of the adeninate anion. Self-aggregation of these ion-pairs is governed by π - π stacking followed by higher order aggregation through coordination to metal cations. The thermodynamic properties for the alkylation of the adeninate anion provide evidence for an entropic bottleneck governing the regio-selectivity at the N9 nitrogen atom. The research on

the adeninate anion stemmed from another research section, the kinetic isotope effect (KIE) of deuterated adenosine triphosphate at the C8 position of the adenyly moiety (C8D-ATP) on *Mycobacterium tuberculosis* shikimate kinase (Mt-SK). In our research we developed a high resolution mass spectroscopy (MS) method to study the KIE of C8D-ATP on Mt-SK. A KIE on V and V/K of 1.5 and 1.4, respectively, were observed showing a secondary isotope effect.