Diaminehalogenoplatinum(II) complex reactions with DMSO

Jens Josephsen
Department of Science and Environment, Roskilde University. P.O. Box 260, DK-4000
Roskilde, Denmark
e-mail: phjens@ruc.dk

DMSO (dimethylsulphoxide) as a solvent has been used in studies of biological effects of several cis-
bis(amine)dihalogenoplatinum(II) complexes in cases where the solubility in water was too low. In
the case of [Pt(n-n)X2] (X=Cl, Br, and I; (n-n)=1,2-ethanediamine (en) and 1,3-propanediamine (tn))
in DMSO solution, the solvent reacts by substituting one halogenide by DMSO over time. The
substitution reactions were followed using changing integrals of signals in NMR-spectroscopy. The
rate constant for [PtenCl2] was found to \(1.1 \times 10^{-4} \text{ s}^{-1}\) at 300 K and from kinetic runs at different
temperatures the energy of activation was estimated as 80 kJ*mol\(^{-1}\).

The rate constant depends on the size of halogenide and was found to increase by a factor of 40 for
[PtenI2] relative to its chloro- analogue. In the tn-series rates were a little faster than in the en-series.
The relative rates when varying the halogenide as leaving group was opposite to that found for the
substitution of halogenide by pyridine in [PtdienX]\(^+\) in aqueous solution.

![Figure 1: Amine-proton signals in 1H-NMR spectra (Bruker AC 250 at 300K) (Δt=10 min.)
during solvolysis of PtenCl2 in DMSO (C\(\text{Pt}\)=.15M). Disappearing signals to the right (staying
at 5.3 ppm); appearing signals to the left. The positions of the last two signals extrapolated
back to \(t=0\) coincides with those observed for [PtenCl(DMSO)]ClO\(_4\)]

The products [Pt(n-n)DMSOX]X were easily isolated, and the DMSO exchange (in DMSO) was
found to be slightly slower than the solvolysis reactions in the en-series, again with iodide giving
rise to the most labile system.

It is easily observed in Fig. 1, that the positions of the emerging signals (of the non-equivalent
amine protons in the product) change. This change was taken as evidence of ion pair formation in
DMSO solution of [Pt(n-n)DMSOX]\(^+\)X \(^-\) in fast equilibrium with the solvated ions. Among the six
[Pt(n-n)DMSOX]X studied here, ion pair formation was found to be modest to almost negligible
with a formation constant of 30 M\(^{-1}\) in the case of [PtenDMSOCI]Cl as the largest.