**Appendix B**

Derivation of rate-law expression for the Ag(I)-catalyzed reaction,

According to the suggested mechanistic Schemes 2 and 3,

Rate =  = *k*2[C2][Ce(OH)3+] (B1)

*K*OH=  , [Ce(OH)3+] =  (B2)

*K*2=  , [C2] = *K*2[Gln][Ag(I)] (B3)

Substituting Eq. (B3) into Eq. (B1) leads to,

Rate =  (B4)

The total concentration of Gln is given by:

[Gln]T = [Gln]F + [C2] (B5)

Substituting Eq. (B3) into Eq. (B5) and rearrangement gives,

[Gln]T = [Gln]F + *K*2[Gln][Ag(I)] = [Gln]F (1+ *K*2[Ag(I)]) (B6)

Therefore,

[Gln]F = (B7)

In view of low [Ag(I)], the second denominator term *K*2[Ag(I)] in the above equation is neglected. Therefore,

[Gln]F = [Gln]T (B8)

Also,

[Ce(IV)]T = [Ce4+]F + [Ce(OH)3+] (B9)

Substituting Eqs. (B2) and (B3) into Eq. (B9),

[Ce(IV)]T = [Ce4+]F +  (B10)

[Ce(IV)]T = [Ce4+]F (1 + ) (B11)

[Ce4+]F = (B12)

Also,

[Ag(I)]T = [Ag(I)]F + [C2] (B13)

[Ag(I)]T = [Ag(I)]F + *K*2[Gln][Ag(I)] = [Ag(I)]F(1 *+ K*2[Gln]) (B14)

[Ag(I)]F = (B15)

Substituting Eqs. (B8), (B12) and (B15) into Eq. (B4) (and omitting ‘T’ and ‘F’ subscripts) leads to,

Rate =  =  (B16)

Under pseudo-first order condition, the rate-law can be expressed by Eq. (B17),

Rate = = *k*C[Ce(IV)] (B17)

Comparing Eqs. (B16) and (B17), the following relationship is obtained,

*k*C =  (B18)

and with rearrangement, the following equations are obtained,

 (B19)

 (B20)