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The Kinetics of Complex Formation between Silver(I) Ions and Diphenylmethylene Bismercaptoethanol in Aqueous Solution. A Slow Substitution at Silver

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Very few kinetic studies of substitution at the silver(I) ion have been reported [1, 2] These studies, which refer to aqueous solutions, suggest that the rates of such substitutions involving displacement of water are very fast indeed We now report on the reaction between diphenylmethylene bis-mercaptoethanol (A) and silver(I) ions in water This reaction involves rates *ca* 10^7-fold slower than those reported in previous studies, which concern particularly the ligands thiosulphate and 1,10-phenanthroline

Detailed kinetic and product analyses show that A ($2\ 5 \times 10^{-5}$ *M*) and silver(I) ions ($\geqslant 2\ 5 \times 10^{-4}$ *M*, added as $AgClO_4$) react as follows (coordinated water molecules have been omitted for simplicity)

$$\mathrm{A} + \mathrm{Ag}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1\ 1\text{-complex}\quad K = k_1/k_{-1} \qquad (1)$$

$$1\ 1\text{-complex} + \mathrm{Ag}^+ \rightleftharpoons 1\ 2\text{-complex} \qquad (2)$$

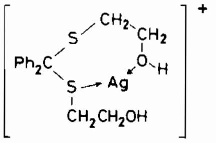
$$1\ 2\text{-complex} + 3H_2O \longrightarrow Ph_2C{=}O + 2AgSCH_2CH_2OH + 2H_3O^+ \qquad (3)$$

The reactions were normally conducted at a constant ionic strength of 0 05 *M* (added $NaClO_4$) and are unaffected by the presence of acid ($HClO_4$, 10^{-4} – 0 10 *M*) By comparison with equilibria (1) and (2), the decomposition (3) is very slow The equilibrium position for (2) lies far to the left Equilibrium (1), our present concern, can therefore be studied with little interference from reactions (2) and (3) The 1 1-complex has ϵ = 13,600 at 254 nm, where A has ϵ = 3,400 The establishment of equilibrium (1) can be followed by stopped-flow spectrophotometry ($k_{obs} = k_1[Ag^+] + k_{-1}$) and the values of D_∞ (final absorbance) at various silver ion concentrations lead to a value for K (= k_1/k_{-1}) We find K = 900 ± 90 M^{-1}, k_1 = 750 ± 50 $M^{-1}s^{-1}$ and k_{-1} = 0 84 ± 0 14 s^{-1} at 25 °C For the thiosulphate ion the rate constant analogous to k_1 is reported to be $>10^9$ $M^{-1}s^{-1}$ at 25 °C and that for 1,10-phenanthroline is probably similarly large [1, 2] The basicity of A can be estimated [3, 4] to be (very approximately) 10^{11}–10^{12} times smaller than that of these other ligands (at least towards the proton) so that the factor of about 10^7 in the forward rate constant appears reasonable if an associative mechanism obtains for the substitution Our results therefore point to such a mechanism at silver(I) and represent the first clear evidence for it

Experiments with other thioacetals and with other metal ions, to be detailed in our full report of this work, suggest that the 1 1-complex has the chelated structure, B

$Ph_2C(SCH_2CH_2OH)_2$

(A)



(B)

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