Kinetic Study of the Methanolysis of Two Dibromocyclopropanes: Second-order Catalysis by Silver Ion

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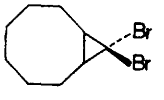
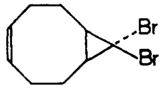
Summary The silver ion-assisted methanolyses of 9,9-dibromobicyclo[6.1.0]nonane (**1**) and 9,9-dibromobicyclo-[6.1.0]non-4-ene (**2**) show both first- and second-order dependence on silver(I) ion; the rate of methanolysis of the olefinic substrate (**2**) is an order of magnitude greater than that of (**1**) while for both substrates the ratios of rate constants first- and second-order in silver are close to 1 : 10

SILVER ions show notable ability in the displacement of halogens from organic molecules under mild conditions.[1] Recently, silver has also been shown to participate in the rearrangement reactions of a variety of halogen-free, small-ring compounds and particularly of cyclopropanes.[2] It thus appeared that the preparatively useful, silver ion-assisted solvolyses of several bicyclic bromocyclopropanes[3,4] might be susceptible to bifunctional catalysis by silver ions. To this end, the dibromocarbene adducts, (**1**) and (**2**), of *cis*-cyclo-octene and cyclo-octa-1,5-diene were selected for kinetic investigation in view of the fast, quantitative, and stereospecific nature of their solvolyses in methanol.[4,5] We now report the predominance of bifunctional catalysis by silver(I) for the methanolysis of both these compounds.



(1)



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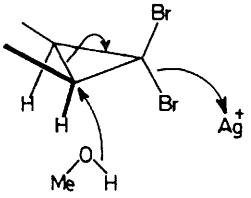

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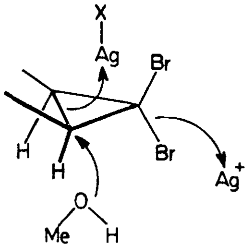

(4)

Solvolyses of **(1)** and **(2)** were carried out in anhydrous methanol at 298 K under pseudo-first-order conditions with respect to substrate† at constant perchlorate concentration‡ and with $AgClO_4$ concentrations from 0·02 to 0·84M. The observed rate constants showed a greater than first-order dependence on silver ion concentration while the apparent second-order rate constant showed an excellent linear relationship to the concentration of silver. A reaction zero-order in silver was not detected. The reaction rate was enhanced by increasing concentration of ClO_4^-‡ at constant silver concentration, an effect which was most pronounced at higher concentrations of silver(I).

Linear regression analysis of these data according to equation (1) provided values of the second- and third-order rate constants as follows: **(1)** $k_2 = 2{\cdot}1 \pm 0{\cdot}5 \times 10^{-4}$ l mol^{-1} s^{-1}, $k_3 = 2{\cdot}5 \pm 0{\cdot}1 \times 10^{-3}$ l^2 mol^{-2} s^{-1} (μ = 1M); and **(2)** $k_2 = 5{\cdot}5 \pm 0{\cdot}3 \times 10^{-3}$ l mol^{-1} s^{-1}, $k_3 = 6{\cdot}3 \pm 0{\cdot}2 \times 10^2$ l^2 mol^{-2} s^{-1} (μ = 0·3 M).

$$k_{obs} = k_2[Ag^+] + k_3[Ag^+]^2 \qquad (1)$$

The simplicity of analysis of these data contrasts strongly with that of previous kinetic investigations of reactions between alkyl halides and silver salts which, in general, have produced complex rate laws with non-integral dependence on silver.[6,7]§ That part of the reaction of **(1)** and **(2)** which is first-order in silver ion appears to be an unexceptional case of electrophilic catalysis of departure of the *exo*-bromine atom, similar to that described for other alkyl bromides,[7] as represented in **(3)**.

The reaction which is second order in silver(I) can be interpreted simply as departure of bromine assisted by two silver cations with the influence of perchlorate concentration attributed to a salt effect. On the other hand, it may signal a process in which the electrophilic action of one silver cation is complemented by involvement of silver(I) in the skeletal rearrangement either as a cation or as an ion pair **(4)**. Such a process can be expressed by equation (2) which provides an equally good fit to the data providing that $AgClO_4$ association is smaller in methanol than has been observed[8] in benzene.

$$k_{obs} = k_2[Ag^+] + k_3'[Ag^+][AgClO_4] \qquad (2)$$

Although calculations based on the same data show that the equilibrium, $2Ag^+ + ClO_4^- \rightleftharpoons Ag_2ClO_4^+$, can also be used to account for the observed third-order term, there appears to be no precedent for such complex ion formation in the case of $AgClO_4$. Nonetheless, it is clear that further investigation is required to resolve this novel mechanistic problem.

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† All reactions were followed through three half-lives, their end-points were determined after ten half-lives, and all showed good pseudo-first-order kinetic behaviour. Products analysed were wholly in agreement with those previously described.[4]

‡ Perchlorate concentration was maintained by the addition of anhydrous $NaClO_4$ in MeOH.

§ Since the completion of this work, R. D. Bach and C. L. Willis (*J. Amer. Chem. Soc.*, 1975, **97**, 3844) have reported that the methanolysis of 2-bromo-octane shows only second-order dependence on Ag^+.

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