# Evidence Against Ion-pair Formation in the Reactions of Ethyl Halides with Silver Salts

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Contrary to a previous report, the product ratio from the reaction of ethyl iodide with silver nitrate in ethanol varies with the salt concentration; the product ratios obtained are very similar to those for the corresponding $S_{\rm N}2$ reactions of triethyloxonium hexafluorophosphate.

For many years, reactions of alkyl halides in the presence of silver ion were always formulated in terms of a rate-determining step consisting of a silver-ion-assisted heterolysis of the carbon–halogen bond;[1] for substitution this was designated as an $S_{\rm N}1{\rm Ag}^+$ reaction. When evidence for nucleophilic assistance by the counter-ion ($X^-$) was found in several systems, the concept of intermediate carbocation formation was retained and these reactions were formulated as proceeding *via* rate-determining formation of either $X^-R^+$ ion-pair intermediates[2,3] or $X^-R^+Hal^-Ag^+$ quadruple-ion intermediates.[4,5]

The argument in favour of ion-pair intermediates in the reactions of alkyl iodides with silver perchlorate in acetonitrile[2] was based upon the assumption that covalently bonded alkyl perchlorates would be unreactive towards the solvent. The subsequent observation that methyl perchlorate is solvolysed relatively rapidly in acetonitrile[6] renders the argument invalid. The only other observation which can be considered to support[2,4] carbocation containing intermediates in silver-ion-assisted reactions of methyl or ethyl halides is the report of *both* a kinetic dependence on nitrate-ion concentration[7,8] and an ethyl ether to ethyl nitrate product ratio independent of nitrate-ion concentration[7] (little, if any, ethylene was formed[8]) in the reaction of ethyl iodide with silver nitrate in ethanol.

However, considerable evidence has accumulated indicating that solvolyses of methyl[9–11] and ethyl[12–14] derivatives are best considered as classical $S_{\rm N}2$ processes, even when very good leaving groups are present. Also, as regards the degree of bonding to an attacking arenesulphonate ion at the transition state, silver-ion-assisted reactions of methyl iodide are identical in character to reactions of other methyl derivatives with very good leaving groups.[15,16] Since there is no evidence for carbocation formation in related systems, we have reinvestigated the product partitioning from the reaction of ethyl iodide with silver nitrate in ethanol and, further, we have compared these values with those obtained using triethyloxonium hexafluorophosphate, a substrate which has been used as a standard in the setting up of a scale of solvent

**Table 1.** Percentage of reaction diverted to nitrate ester as a function of the concentration of added nitrate salt in the ethanolysis of 0.0038 M triethyloxonium hexafluorophosphate or ethyl iodide.[a]

| [Salt]/M | TBAN[b] and $Et_3O^+$ at 0.0 °C | $AgNO_3$ and $Et_3O^+$ at 0.0 °C | $AgNO_3$ and EtI at 20 °C[c] |
|---|---|---|---|
| 0.0040 | 14.1 | 13.4 | 17.3[d] |
| 0.0080 | 21.1 | 23.0 | 24.1 |
| 0.0120 | 28.5 | 28.4 | 28.6 |
| 0.0160 | 33.3 | 31.5 | 31.2 |
| 0.0200 | 35.5 | 34.1 | 33.0 |
| 0.0400 | 44.2 | 40.8 | 37.6 |
| 0.0800 | 50.6 | 47.6 | 41.0 |

[a] Values quoted are in each case the average of six closely agreeing measurements, equally divided between two independent reaction mixtures. [b] Tetra-n-butylammonium nitrate. [c] Burke and Donnan (ref. 7) reported, at 24.5 °C, values of 29.4, 29.9, and 30.0 at initial concentrations of both ethyl iodide and silver nitrate of 0.0125, 0.0250, and 0.0500 M, respectively. [d] After 43 days.

nucleophilicities[14] and which is of the same charge type as the $EtIAg^+$ complex.

The product ratio at complete reaction was determined by comparison of the acid formation in the presence of nitrate ion with that in its absence, 0.08 M silver trifluoromethanesulphonate being then used to assist the ethyl iodide reaction. Measurements were made after a period of >1 h for reactions of $Et_3O^+PF_6^-$ at 0 °C and after 36 days for the silver-ion-assisted reactions of EtI at 20 °C; the ratios did not change when considerably longer times than those needed for complete reaction were employed. The results are presented in Table 1.

It can be seen that not only does the percentage of nitrate ester formed from ethyl iodide vary with the silver nitrate concentration but, also, the values are very similar to those for the identical reactions of the triethyloxonium ion, which are well established[14] as being $S_N2$ in character. The $S_N2Ag^+$ scheme in reactions (1) and (2a, b) can rationalize both the overall kinetics[4,7,8] and the nature of the product partitioning.

$$EtI + Ag^+ \rightleftharpoons EtIAg^+ \qquad (1)$$

$$EtOH + EtIAg^+ \xrightarrow{\text{slow}} Et_2OH^+ + AgI\downarrow \qquad (2a)$$

$$NO_3^- + EtIAg^+ \xrightarrow{\text{slow}} EtONO_2 + AgI\downarrow \qquad (2b)$$

The complex relationship between the product ratio and the silver nitrate concentration follows, largely, from the kinetics of step (2b) being complicated both by electrostatic interactions[17] and, at higher concentrations, by ion-pairing effects within the silver nitrate.[18]

We conclude that no valid evidence exists for the rate-determining formation of ion-pair (or quadruple-ion) intermediates in silver-ion assisted reactions of methyl or ethyl halides and these reactions should be formulated[15] as $S_N2Ag^+$. The complexing of an alkyl halide by silver ion leads to a much better leaving group but, as with other good leaving groups, the structure of the attached alkyl group is of paramount importance in deciding whether the tendency is towards $S_N1$ or $S_N2$ reaction.

*Received, 10th June 1983; Com. 767*

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