

Evidence for an Alkyl Halide-Silver Ion Complex in an S_NAg^+ Reaction

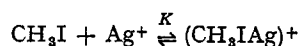
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FOR many years, reactions of alkyl halides assisted by silver ion were considered only in terms of an S_NAg^+ mechanism.¹ Reactions are now known which proceed with simultaneous electrophilic (silver ion) and nucleophilic assistance and opinions have varied as to whether this type of reaction should be formulated as termolecular^{2,3} or as a bimolecular attack upon an alkyl halide-silver ion complex.^{4,5} Also, if reactions with a rate-determining nucleophilic assistance proceed *via* an alkyl halide-silver ion complex, it appears probable that many, if not all, of the reactions formulated as S_NAg^+ also involve such a complex.

We have investigated the reaction of methyl iodide with silver perchlorate in nitromethane and

nitrobenzene and have found that, for a given concentration of silver perchlorate, the reaction rate increases less than linearly with methyl iodide concentration and, at high concentrations, a limiting rate is approached. A limiting rate would not be expected if one feature of the mechanism was the bringing together of an alkyl halide molecule and a silver ion within the rate-determining step. It is, however, consistent with a scheme in which all reaction proceeds through a pre-equilibrium concentration of an alkyl halide-silver ion complex. The experimental results can be correlated with a pre-equilibrium:



TABLE

Correlation of experimental and calculated initial first-order rate coefficients (for production of silver iodide) with respect to silver perchlorate, $k_1(\text{sec.}^{-1})$, for reaction with methyl iodide in nitromethane or nitrobenzene at 25.0°.

$[\text{CH}_3\text{I}]$	$[\text{CH}_3\text{I}Ag^+]^a$	Found	$10^6 k_1$ Calculated ^c
(i) In Nitromethane ($[\text{AgClO}_4] = 0.0341 \text{ M}$):			
∞	0.0341	(5.7) ^b	
0.440	0.0262	4.8	4.4
0.330	0.0243	4.1	4.1
0.223	0.0212	3.5	3.5
0.162	0.0183	3.1	3.1
0.112	0.0161	2.7	2.7
0.0558	0.0093	1.57	1.55
0.0279	0.0052	0.85	0.88
0.0134	0.0027	0.50	0.45
(ii) In Nitrobenzene ($[\text{AgClO}_4] = 0.0172 \text{ M}$):			
∞	0.0172	(15.2) ^b	
0.444	0.0158	14.3	13.7
0.222	0.0150	13.5	13.0
0.112	0.0133	11.3	11.5
0.0558	0.0106	8.8	9.1
0.0279	0.0073	6.3	6.3
0.0134	0.0042	3.7	3.6
0.0069	0.0025	2.05	1.95

^a Calculated using a value for the association constant, K , of 8.1 l. mole⁻¹ in CH_3NO_2 and 35 l. mole⁻¹ in $\text{C}_6\text{H}_5\text{NO}_2$.

^b Designated $k_1\infty$ and obtained from the extrapolation of a plot of reciprocal k_1 against reciprocal $[\text{CH}_3\text{I}]$ to zero reciprocal $[\text{CH}_3\text{I}]$.

^c k_1 (calculated) = $k_1\infty[\text{CH}_3\text{I}Ag^+]/[\text{AgClO}_4]$.

A value for the limiting rate is obtained by extrapolation of the experimental data and a value for the association constant, K , is then chosen so as to give the best fit between experimental and calculated rates over a wide range of methyl iodide concentration (Table).

The higher association constant for interaction

between silver ions and methyl iodide in nitrobenzene, relative to nitromethane, suggests a weaker solvation of the silver ion, a view which is supported by a considerably lower solubility of the silver perchlorate and an increased ionic association as indicated by conductivity measurements.⁶

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¹ See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953, pp. 357—360.

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