each of the species in the reaction mixture were determined by solution of the following equations.

$$\text{mole} \% \; 2 = \text{area } C$$
$$\text{mole} \% \; (1 + 10) = \text{area } A$$
$$\text{mole} \% \; 10 = \text{area } A - 2 \,(\text{area } B)$$
$$\text{mole} \% \; [^2/_3 \,(3 + 9)] = \,^2/_3 \,(\text{area } D)$$
$$\text{mole} \% \; \text{deuterium incorporated} = \text{mole} \% \,(9 + 10) = 1.0 - \text{area } (A + B + C + D)$$

Known mixtures of 1, 2, 3, 9, and 10 were analyzed by this procedure and good agreement was obtained among separate determinations; the probable error was ±1.5%. Analyses of reaction mixtures were also carried out by the use of weighed amounts of both DSS and maleic acid as internal standards. Use of either the Si–CH₃ or vinylic proton signals of these materials as references gave results which agreed with those of the normalization technique within experimental error. The same techniques were also used for the study of the hydrolysis of 10 in H₂O with NaOH.

*Large-Scale Hydrolysis.* A solution of 15.0 g. (0.13 mole) of 1 in 100 ml. of D₂O containing 1.00 mole of NaOD was held at 80° for 4 hr. The reaction mixture was acidified with excess concentrated hydrochloric

acid, evaporated to dryness, and extracted with ethyl alcohol following the established isolation procedure.[1] The alcoholic extract was concentrated at 70° (0.1 mm.) to a viscous liquid residue. Thionyl chloride (29.0 g., 0.25 mole) was added with stirring to the liquid residue; a large amount of hydrogen chloride was evolved and the reaction temperature rose to 55°. The reaction mixture was distilled to yield methylphosphonic dichloride, b.p. 105–110° (100 mm.), m.p. 30–31° (lit.[1] m.p. 30–32°). A solution of the dichloride in 100 ml. of methanol containing 0.5 mole of pyridine was refluxed for 8 hr. The solution was concentrated under reduced pressure, diluted with water, and extracted with ether. After drying over sodium sulfate, the ethereal solution was concentrated and distilled to give 10.7 g. (66.4%) of dimethyl methylphosphonate (12) which was identified by infrared, p.m.r., and gas–liquid chromatographic comparisons with an authentic sample. The ratio of the integrated intensities of the O–CH₃ ($\tau$ 6.33, $J_{PH}$ = 10.8 c.p.s.) and P–CH₃ ($\tau$ 8.59, $J_{PH}$ = 17.4 c.p.s.) signals in CCl₄ indicated the presence of 7.5% of the monodeuterated compound. The mass spectrum of this material showed parent peaks at $m/e$ 124 (major), 125 (minor), 126 (trace), and 127 (trace) attributable to 12, 12-$d_1$, 12-$d_2$, and 12-$d_3$, respectively.

# Electrophilic Catalysis in Nucleophilic Substitution and Elimination. III. Conductances of Some Silver and Tetraethylammonium Salts in Acetonitrile and the Kinetics of Reaction of 2-Octyl Bromide with Tetraethylammonium and Silver Nitrates in That Solvent[1,2]

Y. Pocker[3] and D. N. Kevill

*Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London, England. Received January 30, 1965*

In preparation for a kinetic study in acetonitrile in which tetraethylammonium and silver salts were used as reagents, a study was made of the conductance, at kinetically useful concentrations, of AgClO₄, AgNO₃, AgNO₂, Et₄NClO₄, Et₄NNO₃, and Et₄NNO₂ and of the equimolar mixtures AgNO₃–Et₄NNO₃ and AgNO₂–Et₄NNO₂. The respective dissociation constants M⁺X⁻ ⇌ M⁺ + X⁻ were obtained by a Fuoss–Shedlovsky treatment. Of the six salts mentioned above only silver nitrite behaves abnormally in that for concentrations above $2 \times 10^{-3}$ M there is little variation in the equivalent conductance as concentration is varied. The dominant dissociation of silver nitrite in the range 0.002–0.16 M is explained in terms of the following equilibrium: $2Ag^+NO_2^- \rightleftharpoons Ag^+ + Ag(NO_2)_2^-$. The

kinetics of the reaction of 2-octyl bromide with nitrate ions supplied (a) as Et₄NNO₃, (b) as AgNO₃, and (c) as mixtures of Et₄NNO₃–AgNO₃ have been investigated, and the olefin proportion of the products has been determined. The extent of heterogeneous catalysis by silver bromide produced during the reaction with AgNO₃ is relatively unimportant. The reaction kinetics and the olefin proportion of the products have also been determined for the reaction of 2-octyl chloride and 1-octyl bromide with silver nitrate in acetonitrile. The reaction of 2-octyl bromide with Et₄NNO₃ is a reversible bimolecular nucleophilic substitution with practically no elimination accompanying it. The proposed mechanistic scheme for silver nitrate catalysis involves the formation of an alkyl halide–silver ion complex. The subsequent reaction of this complex is rate determining. Anionic assistance (i.e., intervention by $NO_3^-$) is shown to occur within this rate-determining step. The more detailed nature of this nucleophilic assistance requires that rates and products are determined by two different steps.

(1) Part II: Y. Pocker, *J. Chem. Soc.*, 1972 (1960).
(2) Taken from part of the thesis presented by Dennis N. Kevill in partial fulfillment of the requirements for the Ph.D. Degree, University of London, Jan. 1960.
(3) To whom inquiries should be directed. Department of Chemistry, University of Washington, Seattle, Wash. 98105.

## Introduction

Kinetic information relating to electrophilic assistance by metallic cations in replacement reactions of alkyl halides is confined to mercuric ions[4-6] and to silver ions.[7-21]

Interpretation of the kinetics of mercuric ion assisted reactions in terms of mechanism proved difficult because of the existence in solution of several electrophilic species.[4,5] We thought therefore that it would be simpler to elucidate first the mechanisms of reaction in which the electrophilic assistance is by a univalent silver ion in the presence of univalent anions.

Where $S_N1$ reactions lead through the isomerization of the carbonium ion to rearranged products, while $S_N2$ substitutions give normal products, the silver ion reaction has been shown to yield rearranged products. Although inversion of optical activity is usually greater in silver ion assisted substitution reactions than in $S_N1$ reactions, Masterman, Hughes, and Ingold[22] argued that the general pattern observed in the former was nevertheless that expected for reactions proceeding *via* a carbonium ion intermediate. Realizing however that these two step reactions are not necessarily true $S_N1$ processes they labeled the silver ion assisted reactions as $S_N1-Ag^+$.

The relative rates which have been observed for the silver ion assisted reactions of primary alkyl halides are intermediate between those that one might predict for unimolecular ($S_N1-E1$) processes and those observed in the classic examples of the limiting bimolecular ($S_N2$) processes. In particular one might stress the low reactivity of isobutyl and neopentyl bromides and iodides with silver nitrate,[15,21] silver nitrite,[19] and silver perchlorate.[21]

The present investigation was initiated in an effort to attain a better understanding of the mechanisms operative in silver ion assisted substitutions. Of the solvents which give stable solutions of both silver salts and alkyl halides, acetonitrile has the further advantage of being rather inert toward carbonium ions formed within it; it will react with these only if the anions present in solution are very weak nucleophiles.[23]

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(19) For a detailed review see N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).
(20) J. A. Vona and J. Steigman, *ibid.*, **81**, 1095 (1959).
(21) For an excellent paper on ion-pair formation in the reactions of alkyl iodides with silver salts see G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *ibid.*, **82**, 704 (1960).
(22) E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1236 (1937).
(23) G. W. H. Cheesman, *Chem. Ind.* (London), 281 (1954); S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, 76, 4468 (1954).
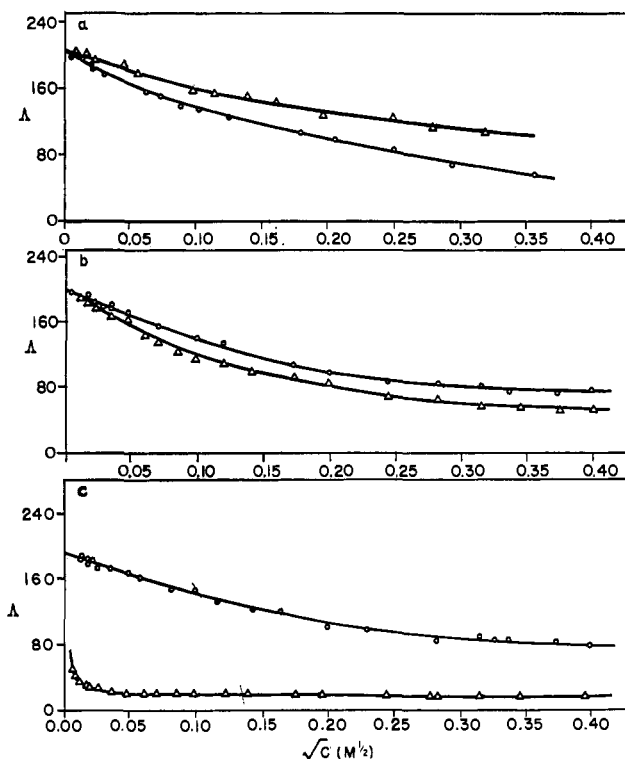
Figure 1. Onsager plots of conductivities in $CH_3CN$ at 25.0°: (a) △, $AgClO_4$, $\alpha_{expt}/\alpha_{theor} = 1.28$; O, $Et_4NClO_4$, $\alpha_{expt}/\alpha_{theor} = 2.12$; (b) △, $AgNO_3$, $\alpha_{expt}/\alpha_{theor} = 2.56$; O, $Et_4NNO_3$, $\alpha_{expt}/\alpha_{theor} = 1.77$; (c) △, $AgNO_2$; O, $Et_4NNO_2$, $\alpha_{expt}/\alpha_{theor} = 1.35$.

Silver nitrate, perchlorate, and nitrite are remarkably soluble in acetonitrile and their respective solutions show appreciable electrical conductivity (subsequent section); the silver ion must be effectively solvated by acetonitrile and probably forms a definite complex ion, $Ag(NCCH_3)_2^+$.

When facing the problem of interpreting solution kinetics, it is important to know the condition of the cationic and anionic reagents. We therefore felt it necessary first to study the electrochemistry of the principal salts which were to be used in this kinetic work, not only alone but also as mixtures. Quite a number of investigations of the conductivity of silver nitrate in acetonitrile have been carried out but only a few included kinetically useful concentrations.[24] The conductivities of silver perchlorate and tetraethylammonium nitrate and perchlorate have been previously reported[24] but not for kinetically useful concentrations in acetonitrile. The conductivities of silver nitrite and tetraethylammonium nitrite have not previously been reported over any concentration range.

## Results

*Conductivities in Acetonitrile.* Onsager plots of the equivalent conductance $\Lambda$ (ohm$^{-1}$ cm.$^2$ mole$^{-1}$) against $\sqrt{C}$ (mole$^{0.5}$ l.$^{-0.5}$) are given in Figure 1. Expressing the Onsager equation as $\Lambda = \Lambda_0 - \alpha\sqrt{C}$, where $\Lambda_0$ is the equivalent conductance at infinite dilution, the theoretical slope for a univalent electrolyte in solvent acetonitrile at 25.0° can be calculated as $\alpha_{theor} = 0.736\Lambda_0 + 230$. The Onsager equation was

(24) Y. P. Landold-Börnstein, "Zahlenwerte und Funktionen," Part 7, Vol. II, Springer-Verlag, Heidelberg, 1960, pp. 416, 417.

not obeyed for any of the salts considered, and the deviations of the initial slopes from the predicted slopes were considered to be a measure of the relative amounts of ion-pair formation in the various salts when they are at low concentrations. Examination of the Onsager plots shows that silver perchlorate is more dissociated at any concentration than the silver nitrate and also more than tetraethylammonium perchlorate. Silver nitrate is, however, less dissociated at any concentration than is tetraethylammonium nitrate.

It is not possible to extrapolate graphically the values obtained for silver nitrite to infinite dilution, but in view of the fact that $\lambda^0_{Ag^+} = \lambda^0_{NEt_4^+}$ we may safely assume that $\Lambda_{0(AgNO_2)} = \Lambda_{0(NEt_4NO_2)}$. It follows therefore, that even at the lowest measured concentration, i.e., at $3.7 \times 10^{-5}$ $M$ AgNO$_2$, only about 25% of the silver nitrite is actually dissociated. The form of the Fuoss–Shedlovsky equation used in evaluating ion-pair equilibria was $1/\Lambda S = (1/\Lambda_0) + C\Lambda Sf^2/K_S\Lambda_0^2$ where $\Lambda$ is the equivalent conductance at salt concentration $C$; $S$ is the value of the Shedlovsky extrapolation function at concentration $C$, obtainable from values tabulated by Daggett[25]; $\Lambda_0$ is the true value for the equivalent conductance at infinite dilution; $f$ is the activity coefficient for the salt in solution at concentration $C$; $K_S$ is the dissociation equilibrium constant (ion pairs into simple ions). Plots of $1/\Lambda S$ against $C\Lambda Sf^2$ were linear for low salt concentrations, with intercept $1/\Lambda_0$ and slope of $1/K_S\Lambda_0^2$ enabling $\Lambda_0$ and $K_S$ to be deduced (Table I).

Table I. Values for the Dissociation Constants ($K_S$, mole l.$^{-1}$) and Equivalent Conductances at Infinite Dilution[a]

| Salt | $\Lambda_0$ | $10^2 K_S$ |
|------|------|------|
| AgClO$_4$ | 203 | 4.3 |
| AgNO$_3$ | 199 | 0.9 |
| NEt$_4$ClO$_4$ | 203 | 1.7 |
| NEt$_4$NO$_3$ | 199 | 2.1 |
| NEt$_4$NO$_2$ | 187 | 4.0 |

[a] $\Lambda_0$, ohm$^{-1}$ cm.$^2$ mole$^{-1}$, obtained by a Fuoss–Shedlovsky treatment of the conductance of several salts in acetonitrile at 25.0°.

Silver nitrite behaves abnormally in that for concentrations above $2 \times 10^{-3}$ $M$ there is little variation in the equivalent conductance as concentration is varied. Consequently, the simple dissociation Ag$^+$NO$_2^-$ $\overset{K_1}{\rightleftharpoons}$ Ag$^+$ + NO$_2^-$ cannot be operative. A clue comes from the stability of the complex anion Ag(NO$_2$)$_2^-$ which is known to exist and the corresponding cesium and potassium salts of this anion have been reported.[26] Accepting the dominant dissociation in the range 0.002–0.16 $M$ to be 2Ag$^+$NO$_2^-$ $\overset{K_2}{\rightleftharpoons}$ Ag$^+$ + Ag(NO$_2$)$_2^-$ one obtains [Ag$^+$] $\cong$ [Ag(NO$_2$)$_2^-$] = $K_2^{0.5}$[AgNO$_2$]. When the degree of dissociation is small, the number of ions is proportional to the stoichiometric concentration of AgNO$_2$ leading to $\Lambda \approx$ constant in accord with the experimental observations (Figure 1c).

The equimolar mixture AgNO$_3$–Et$_4$NNO$_3$ gives at any concentration an equivalent conductance equal to

or, if anything, slightly higher than that obtained by taking the mean value of the conductivities of the separate components at that concentration. In contrast, the conductance of the equimolar mixture of silver nitrite and tetraethylammonium nitrite varies in such a way that it could be due either to tetraethylammonium ions and nitrite ions alone with silver nitrite present in a nonconducting form (molecules or ion pairs) or alternatively to tetraethylammonium ions and Ag(NO$_2$)$_2^-$, the latter being in accord with the proposed ionization scheme for silver nitrite. These results may also be considered with those of a preliminary survey of the vapor pressure of acetonitrile in such solutions. We find that silver nitrite lowers the vapor pressure of acetonitrile less than does an equivalent amount of tetraethylammonium nitrite. Further, an equimolar mixture of AgNO$_2$–Et$_4$NNO$_2$ lowers the vapor pressure of acetonitrile by the same amount as does Et$_4$NNO$_2$ alone indicating that the equimolar mixture behaves like a univalent electrolyte. This behavior accords with the suggested stability of Ag(NO$_2$)$_2^-$ in acetonitrile solvent.

*Kinetic Results. A. "Solvolysis" of 2-Octyl Bromide by CH$_3$CN.* The rate of bromide ion production, d[Br$^-$]/d$t$, from solutions of 2-octyl bromide in acetonitrile is measurably fast at 100.01°. The first-order rate coefficients $(1/[RBr])$ d[Br$^-$]/d$t = k_1$ increase linearly up to about 15% reaction, the value of the coefficient then starts to fall, due to a movement towards equilibrium. The observed autocatalysis is probably due to electrophilic catalysis by the HBr produced during the reaction. By considering initial values for the first-order coefficient, effects due to this autocatalysis are minimized; mean initial $k_1 = 15.4 \times 10^{-8}$ sec.$^{-1}$ of which ca. 84 ± 2% is elimination and 16 ± 2% proceeds through substitution reaction with the solvent.

*B. Reaction of 2-Octyl Bromide with Et$_4$NNO$_3$.* The reaction of 2-octyl bromide with tetraethylammonium nitrate in acetonitrile, at 72.9°, as determined by bromide ion production, has been found to be second order, first order in each reactant: $V = k_2[RBr][Et_4NNO_3]$. There was no evidence of any first-order contribution to the rate. Bromide ions supplied as tetraethylammonium bromide were found to have no effect on the value of the initial second-order rate coefficient. Because the reaction moves

Table II. Initial Second-Order Rate Coefficients[a]

| Temp., °C. | [NEt$_4$NO$_3$], $M$ | [NEt$_4$Br], $M$ | [2-Oct.Br], $M$ | $10^5 k_2^i$ |
|------|------|------|------|------|
| 44.6 | 0.0513 | ... | 0.0515 | 0.45 |
| 63.8 | 0.0498 | ... | 0.0500 | 3.05 |
| 72.9 | 0.0359 | ... | 0.0181 | 7.3 |
| 72.9 | 0.0359 | ... | 0.0722 | 7.0 |
| 72.9 | 0.0359 | ... | 0.0361 | 7.2 |
| 72.9 | 0.0359 | 0.00456 | 0.0361 | 7.4 |
| 72.9 | 0.0359 | 0.00912 | 0.0361 | 7.4 |
| 72.9 | 0.0718 | ... | 0.0361 | 7.1 |
| 72.9 | 0.0180 | ... | 0.0361 | 7.3 |
| 86.5 | 0.0531[b] | ... | 0.0533[b] | 21.3[b] |

[a] $k_2^i$ (l. mole$^{-1}$ sec.$^{-1}$), for bromide ion production in the reaction of 2-octyl bromide with tetraethylammonium nitrate in acetonitrile. $k_2^i = Ae^{-E_a/RT}$; $A = 10^{9.8}$ l. mole$^{-1}$ sec.$^{-1}$, $E_a = 21.4$ kcal. mole$^{-1}$. [b] Quantities uncorrected for solvent expansion from room temperature.

(25) H. M. Daggett, Jr., *J. Am. Chem. Soc.*, **73**, 4977 (1951).
(26) (a) G. S. Jamieson, *ibid.*, **38**, 614 (1907); (b) M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. chim. ital.*, **82**, 413 (1952).

**Table III. Initial 2.5-Order Rate Coefficients[a]**

| Temp., °C. | [AgNO₃], $M$ | [2-Oct.Br], $M$ | $10^8 V_{\text{total}}$ | $10^8 V_{\text{NO}_3^-}$ | $10^8 V_{\text{AgNO}_3}$ | $10^3 k_{2.5}$[b] |
|---|---|---|---|---|---|---|
| 25.0 | | | | | | |
| | 0.0100 | 0.0795 | 3.85 | 0.04 | 3.81 | 0.479 |
| | 0.0199 | 0.0795 | 10.9 | 0.1 | 10.8 | 0.484 |
| | 0.0398 | 0.0795 | 31.5 | 0.2 | 31.3 | 0.496 |
| | 0.0796 | 0.0795 | 85.2 | 0.3 | 84.9 | 0.476 |
| | 0.1561 | 0.0795 | 266 | 0.6 | 265 | 0.525 |
| | | | | | Mean value | 0.492 |
| 44.6 | | | | | | |
| | 0.0193 | 0.0097 | 8.7 | 0.1 | 8.6 | 3.38 |
| | 0.0193 | 0.0193 | 18.0 | 0.2 | 17.8 | 3.44 |
| | 0.0193 | 0.0387 | 34.8 | 0.3 | 34.5 | 3.32 |
| | 0.0193 | 0.0773 | 67.3 | 0.6 | 66.7 | 3.22 |
| | 0.0097 | 0.0193 | 6.0 | 0.1 | 5.9 | 3.20 |
| | 0.0387 | 0.0193 | 49.2 | 0.3 | 48.9 | 3.33 |
| | 0.0773 | 0.0193 | 136 | 0.6 | 135 | 3.25 |
| | 0.0097 | 0.0073 | 25.8 | 0.3 | 25.5 | 3.45 |
| | 0.0387 | 0.0773 | 183 | 1.3 | 182 | 3.09 |
| | 0.0759 | 0.0773 | 510 | 2.5 | 507 | 3.14 |
| | | | | | Mean value | 3.27 |
| 63.8 | | | | | | |
| | 0.0088 | 0.0188 | 90.2 | 1.1 | 89.1 | 18.4 |
| | 0.0376 | 0.0188 | 249 | 2.2 | 247 | 18.0 |
| | | | | | Mean value | 18.3 |
| 72.9 | | | | | | |
| | 0.00226 | 0.0181 | 7.6 | 0.3 | 7.4 | 38.0 |
| | 0.00452 | 0.0181 | 21.7 | 0.6 | 21.1 | 38.4 |
| | 0.00903 | 0.0181 | 66.2 | 1.2 | 65.0 | 41.8 |
| | 0.0181 | 0.0181 | 173 | 2.3 | 171 | 38.8 |
| | 0.0361 | 0.0181 | 441 | 4.6 | 436 | 35.1 |
| | 0.0722 | 0.0181 | 1240 | 9.3 | 1230 | 35.0 |
| | | | | | Mean value | 37.8 |

[a] $k_{2.5}$ (l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$) for silver bromide production in the reaction between 2-octyl bromide and silver nitrate in acetonitrile. [b] The integration of the equation $dx/(a - x)^{1.5}(b - x) = k\,dt$ leads to three different solutions depending on condition (i) $a > b$, (ii) $a = b$, or (iii) $a < b$. The $k_{2.5}$ coefficients evaluated from initial rates were found to be practically identical with those calculated *throughout* any given run using the integrated equations for reactions of order 2.5. Examples are given in the Experimental Section.

toward an unstable equilibrium, the rate coefficients were initial, calculated from measurements up to 10% of the stoichiometrically possible reaction. Over this range, the values were constant (Table II). For each combination of concentrations recorded in Table II, an attempt was made to follow the partial rate of elimination by determining the amount of acid developed. In no case could any acid development be detected, even though measurements were made over periods of up to 57 days.

The equilibrium constant $K$ for the substitution reaction is given by $K = $ [2-Oct.ONO₂][Et₄NBr]/[2-Oct.-Br][Et₄NNO₃]. It was found, however, that owing to a slow side reaction the bromide ion concentration after reaching a maximum fell slowly but steadily. The value of $K$, in the absence of any side reaction, as obtained by extrapolation is *ca.* 0.8 at 72.9°.

*C. Reaction of 2-Octyl Bromide with AgNO₃.* The analytical treatment of the reaction of 2-octyl bromide with silver nitrate was in terms of both initial rates and of integrated rate coefficients. Since the second-order rate coefficients for attack by tetraethylammonium nitrate are known (Table II) or can be deduced from the experimentally determined Arrhenius parameters, one can evaluate *a priori* the contribution to the over-all rate of $V_{\text{NO}_3^-}$, a simple Sₙ2 component arising from the presence of nitrate ions:

$-d[\text{Ag}]^+/dt = V_{\text{total}} = V_{\text{AgNO}_3} + V_{\text{NO}_3^-}$. Such a contribution to the over-all rate is just over 1% at 44.6 and 25.0° and just under 4% at 72.9°. The predominant reaction is due to a silver ion assisted process, and the kinetics of this reaction have been studied at 25.0, 44.6, 63.8, and 72.9°. The initial velocity of the silver nitrate reaction, $V^i_{\text{AgNO}_3}$, is found to be first order in 2-octyl bromide and 1.5 order in AgNO₃: $V^i_{\text{AgNO}_3} = k_{2.5}$[2-Oct.Br][AgNO₃]$^{1.5}$ (Table III). Adopting the Arrhenius equation $k_{2.5} = Ae^{-E_a/RT}$ one obtains (Figure 2) $A = 10^{10.3}$ l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$ and $E_a = $ 18.6 kcal. mole$^{-1}$.

The silver nitrate catalyzed reaction is accelerated by added tetraethylammonium nitrate (Figure 3). The contribution of $V_{\text{NO}_3^-}$ to the over-all rate, $V_{\text{total}}$, is small even in the presence of 0.16 $M$ Et₄NNO₃, much too small to account for the observed rate acceleration produced by added Et₄NNO₃. The effect of adding tetraethylammonium nitrate to a constant concentration of silver nitrate and 2-octyl bromide was to increase significantly $V_{\text{AgNO}_3}$ (Table IV): $k_{2.5}$ was calulated using the equation $V^i_{\text{AgNO}_3} = k_{2.5}$[2-Oct.Br][AgNO₃]{[AgNO₃] + [NEt₄-NO₃]}$^{0.5}$. The $k_{2.5}$ rate coefficients so calculated were found to be practically identical with the ones obtained in the absence of Et₄NNO₃ (compare Tables III and IV). The ratio of substitution to elimination was almost independent of added tetraethylammonium nitrate and

Table IV. Initial 2.5-Order Rate Coefficients[a]

| Temp., °C. | [2-Oct.Br], $M$ | [AgNO₃], $M$ | [NEt₄NO₃], $M$ | $10^8 V_{total}$ | $10^8 V_{NO_3^-}$ | $10^8 V_{AgNO_3}$ | $10^3 k_{2.5}$ |
|---|---|---|---|---|---|---|---|
| 25.0 | | | | | | | |
| | 0.0795 | 0.0100 | 0.0398 | 8.6 | 0.2 | 8.4 | 0.474 |
| | 0.0795 | 0.0199 | 0.0398 | 18.7 | 0.2 | 18.5 | 0.479 |
| | 0.0795 | 0.0398 | 0.0398 | 44.1 | 0.3 | 43.8 | 0.491 |
| | 0.0795 | 0.0796 | 0.0398 | 107 | 0.5 | 106 | 0.485 |
| 44.6 | | | | | | | |
| | 0.0193 | 0.0193 | | 18.0 | 0.2 | 17.8 | 3.44 |
| | 0.0193 | 0.0193 | 0.0107 | 23.0 | 0.3 | 22.7 | 3.53 |
| | 0.0193 | 0.0193 | 0.0193 | 26.9 | 0.3 | 26.6 | 3.63 |
| | 0.0193 | 0.0193 | 0.0193 | 24.1 | 0.3 | 23.8 | 3.25 |
| | 0.0193 | 0.0193 | 0.0214 | 27.2 | 0.4 | 26.8 | 3.54 |
| | 0.0193 | 0.0193 | 0.0385 | 32.1 | 0.5 | 31.6 | 3.53 |
| | 0.0193 | 0.0193 | 0.0387 | 30.7 | 0.5 | 30.2 | 3.37 |
| | 0.0193 | 0.0193 | 0.0799 | 39.6 | 0.8 | 38.8 | 3.31 |
| | 0.0193 | 0.0193 | 0.1200 | 47.5 | 1.2 | 46.3 | 3.33 |
| | 0.0193 | 0.0193 | 0.1600 | 55.1 | 1.5 | 53.6 | 3.40 |
| | 0.0193 | 0.0097 | 0.0290 | 13.1 | 0.3 | 12.8 | 3.47 |
| | 0.0193 | 0.0193 | 0.0193 | 26.9 | 0.3 | 26.6 | 3.63 |
| | 0.0193 | 0.0193 | 0.0193 | 24.1 | 0.3 | 23.0 | 3.25 |
| | 0.0193 | 0.0290 | 0.0097 | 36.3 | 0.3 | 36.0 | 3.27 |
| | 0.0193 | 0.0387 | 0.0000 | 49.2 | 0.3 | 48.9 | 3.33 |
| | 0.0193 | 0.0097 | 0.0387 | 15.1 | 0.4 | 14.7 | 3.57 |
| | 0.0193 | 0.0193 | 0.0385 | 32.1 | 0.5 | 31.6 | 3.53 |
| | 0.0193 | 0.0193 | 0.0387 | 30.7 | 0.5 | 30.2 | 3.37 |
| | 0.0193 | 0.0387 | 0.0387 | 72.8 | 0.6 | 72.2 | 3.46 |
| | 0.0193 | 0.0773 | 0.0387 | 162 | 1.0 | 161 | 3.10 |

[a] $k_{2.5}$ (l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$) for the production of silver bromide.

to a close approximation was a function only of temperature; the proportion of elimination relative to substitution increasing with temperature (Table V).
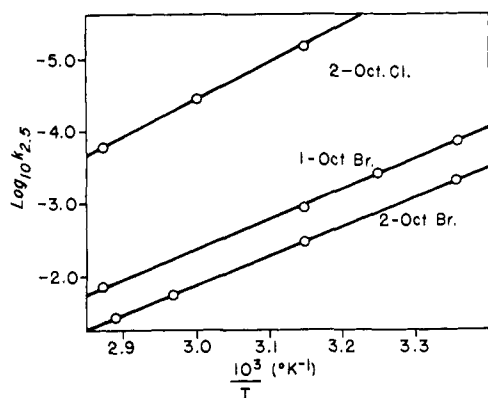


Figure 2. The variation of $k_{2.5}$ with temperature in the reaction of alkyl halides with AgNO₃ in CH₃CN expressed in a conventional Arrhenius plot.

The reaction between 2-octyl bromide and AgNO₃ was also studied in the presence of added Et₄NClO₄ (Figure 3). This salt was found to *depress* the over-all reaction rate, d[Br⁻]/d$t$, while increasing only slightly the percentage of the reaction component leading to elimination. (Table VIa.) This reaction was also carried out in the presence of a large and constant concentration of tetraethylammonium perchlorate in order to test whether, in the limiting case, third-order kinetics of the form $V_{AgNO_3} = k_3[\text{2-Oct.Br}][AgNO_3]^2$, where $k_3$ is a constant, can be obtained. Within the range investigated it was found that the addition of an excess of tetraethylammonium perchlorate raised the formal order in silver nitrate from a value of 1.5 to 1.83 (Table VIb).

*Reaction of 2-Octyl Chloride and 1-Octyl Bromide with AgNO₃.* The reactions of 2-octyl chloride and 1-octyl bromide with silver nitrate in acetonitrile have been investigated at several temperatures, and at each temperature the kinetics have been found to be consistent with the formula $V_{AgNO_3} = k_{2.5}[\text{RX}][AgNO_3]^{1.5}$ such that the 2.5-order rate coefficient, $k_{2.5}$, is a constant at a given temperature. The constancy of the integrated 2.5-order coefficients throughout each run
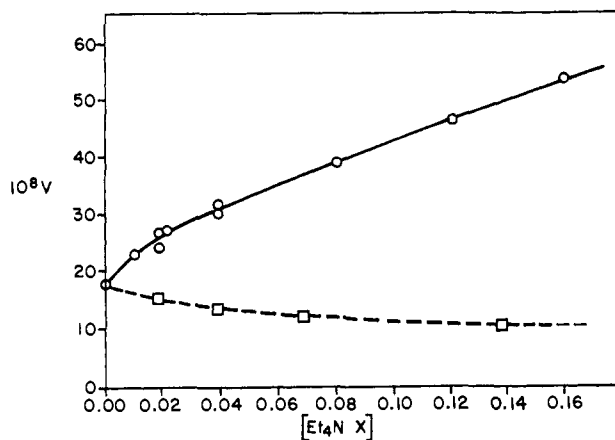


Figure 3. Effect of added Et₄NX on the initial rate of reaction, $V$ (mole l.$^{-1}$ sec.$^{-1}$), of 2-octyl bromide (0.0193 $M$) with AgNO₃ (0.0193 $M$) in CH₃CN at 44.6°: O, Et₄NNO₃; □, Et₄NClO₄.

up to at least 40% reaction indicates that in these reactions the precipitated silver halide has no observable catalytic activity. It was found that the reaction proceeding through elimination is a constant proportion of the over-all process and that 1-octyl bromide leads to only very small amounts of olefin. As with 2-octyl bromide, a slight increase in the olefin proportion as the concentration of silver nitrate was increased

<div style="display: flex">

**Table V.** The Olefin Proportion in the Reaction with Silver Nitrate

| Temp., °C. | [2-Oct.Br], M | [AgNO₃], M | [NEt₄NO₃], M | % reaction followed[a] | % elimination |
|---|---|---|---|---|---|
| 25.0 | 0.0795 | 0.0796 | ... | 40 | 6.5 |
| 25.0 | 0.0795 | 0.0398 | 0.0398 | 25 | 5.9 |
| 44.6 | 0.0194 | 0.0387 | ... | 80 | 8.1 |
| 44.6 | 0.0194 | 0.0194 | 0.0389 | 30 | 8.2 |
| 44.6 | 0.0194 | 0.0194 | 0.0192 | 50 | 8.0 |
| 44.6 | 0.0194 | 0.0194 | ... | 50 | 7.9 |
| 44.6 | 0.0194 | 0.0097 | ... | 60 | 7.7 |
| 63.8 | 0.0188 | 0.0376 | ... | 70 | 10.6 |
| 63.8 | 0.0188 | 0.0188 | ... | 50 | 10.2 |
| 72.9 | 0.0181 | 0.0361 | ... | 50 | 12.2 |
| 72.9 | 0.0181 | 0.0181 | ... | 30 | 12.1 |
| 100.1[b] | 0.0400 | 0.0200 | ... | 64 | 16.6 |
| 100.1[b] | 0.0200 | 0.0200 | ... | 44 | 16.2 |

[a] Relates to the percentage of the over-all reaction of the 2-octyl bromide for which *both* the hydrogen ion production and the over-all reaction rate have been followed. [b] Not corrected for expansion of solvent from room temperature.

**Table VI.** Effect of Added Et₄NClO₄

(a)

| Temp., °C. | [2-Oct.Br], M | [AgNO₃], M | [Et₄NClO₄], M | $10^8 V$, mole l.⁻¹ sec.⁻¹ | Elimination, % |
|---|---|---|---|---|---|
| 44.6° | 0.0193 | 0.0193 | ... | 18.0 | 7.9 |
| 44.6 | 0.0193 | 0.0193 | 0.0193 | 15.1 | 8.0 |
| 44.6 | 0.0193 | 0.0193 | 0.0387 | 13.5 | 8.3 |
| 44.6 | 0.0193 | 0.0193 | 0.0688 | 12.2 | 8.4 |
| 44.6 | 0.0193 | 0.0193 | 0.138 | 10.9 | 9.3 |

(b[a])

| [AgNO₃], mole l.⁻¹ | $10^2 k_2$ l. mole⁻¹ sec.⁻¹ | $10^2 k_{2.5}$, l.¹·⁵ mole⁻¹·⁵ sec.⁻¹ | $10^2 k_{2.83}$, l.¹·⁸³ mole⁻¹·⁸³ sec.⁻¹ | $10^2 k_3$, l.² mole⁻² sec.⁻¹ |
|---|---|---|---|---|
| 0.00263 | 0.0189 | 0.369 | 2.67 | 7.2 |
| 0.00525 | 0.336 | 0.464 | 2.67 | 6.4 |
| 0.0105 | 0.0618 | 0.604 | 2.76 | 5.9 |
| 0.0210 | 0.145 | 0.735 | 2.66 | 5.1 |

[a] [2-Oct.Br] = 0.0189 $M$; [Et₄NClO₄] = 0.151 $M$; temp. = 60.0°.

was observed at each temperature, and therefore the variation in the olefin proportion of products with temperature was considered for one concentration of silver nitrate (Table VII).

### Discussion

At 100.1° a solution of 2-octyl bromide in acetonitrile was found to produce bromide ions in the absence of any additives. The addition of Et₄NClO₄ at this temperature accelerates this reaction, the effect being in the nature of a positive salt effect on a reaction whose transition state is more polar than its ground state. The reaction of 2-octyl bromide with acetonitrile yields about 85% of olefin irrespective of whether perchlorate salt is present and about 15% of product derived from substitution by solvent. The reaction of 2-octyl bromide in acetonitrile could be a unimolecular ionization to yield a carbonium ion, which then partitions between substitution (SN1) to yield CH₃-C⁺NRBr⁻ and elimination (E1) to yield CH₃C⁺NHBr⁻

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**Table VII.** Initial 2.5-Order Rate Coefficients of Silver Bromide Production[a]

| Temp., °C. | [2-Oct.Cl], M | [AgNO₃], M | $10^6 k_{2.5}^a$ | % elimination | % reaction followed[c] |
|---|---|---|---|---|---|
| 44.6 | 0.0387 | 0.0387 | 7.1 | ... | ... |
| 44.6 | 0.0773 | 0.0773 | 6.9 | 3.3 | 8 |
| 59.7 | 0.0378 | 0.0378 | 35.5 | 4.0 | 14 |
| 59.7 | 0.0378 | 0.0756 | 35.6 | 4.4 | 30 |
| 75.0 | 0.0369 | 0.00231 | 203 | ... | ... |
| 75.0 | 0.0369 | 0.00923 | 204 | 5.3 | 8 |
| 75.0 | 0.0369 | 0.0369 | 176 | 5.4 | 30 |
| 75.0 | 0.0369 | 0.0738 | 167 | 5.7 | 70 |
| 100.1 | 0.0400[b] | 0.0129[b] | 1480[b] | 7.4 | ...[d] |
| 100.1 | 0.0400[b] | 0.0260[b] | 1490[b] | 7.5 | ...[d] |

$k_{2.5} = Ae^{-E_a/RT}$; $A = 10^{11.1}$ l.¹·⁵ mole⁻¹·⁵ sec.⁻¹, $E_a = 23.7$ kcal. mole⁻¹

| Temp., °C. | [1-Oct.Br], M | [AgNO₃], M | $10^3 k_{2.5}^a$ | % elimination | % reaction followed[c] |
|---|---|---|---|---|---|
| 25.0 | 0.0795 | 0.0795 | 0.142 | 0.06 | 60 |
| 34.8 | 0.0784 | 0.0784 | 0.395 | 0.10 | 55 |
| 44.6 | 0.0193 | 0.00193 | 1.10 | ... | ... |
| 44.6 | 0.0193 | 0.00387 | 1.06 | ... | ... |
| 44.6 | 0.0193 | 0.00968 | 1.30 | ... | ... |
| 44.6 | 0.0193 | 0.0193 | 1.30 | ... | ... |
| 44.6 | 0.0193 | 0.0387 | 1.19 | ... | ... |
| 44.6 | 0.0773 | 0.0773 | 1.02 | 0.12 | 70 |
| 75.0 | 0.0369 | 0.0369 | 14.4 | ... | ... |
| 75.0 | 0.0738 | 0.0738 | 13.5 | 0.16 | 55 |

$k_{2.5} = Ae^{-E_a/RT}$; $A = 10^{10}$ l.¹·⁵ mole⁻¹·⁵ sec.⁻¹, $E_a = 18.9$ kcal. mole⁻¹

[a] $k_{2.5}$ (l.¹·⁵ mole⁻¹·⁵ sec.⁻¹) and values for the ratio of hydrogen ions produced to silver bromide produced, $B$, for the reaction of 2-octyl chloride and 1-octyl bromide with silver nitrate in acetonitrile at several temperatures. [b] Values uncorrected for expansion of solvent from 20° to thermostat temperatures. [c] Relates to the percentage of the over-all reaction of alkyl halide for which both the hydrogen ion production and the over-all rate have been followed. [d] At 100.1° it was found that a slow side reaction occurs which reduces the acidity, and consequently, initial values for the olefin proportion were taken.

and a mixture of 1- and 2-octenes; alternatively it could be a bimolecular attack by CH₃CN involving mechanisms SN2 and E2 acting concurrently. Both mechanisms would be consistent with the observed first-order kinetics and since in both mechanisms the transition state is more polar than the ground state, both account equally well for the marked acceleration produced by the addition of Et₄NClO₄.

The reaction of 2-octyl bromide with Et₄NNO₃ in acetonitrile shows second-order kinetics, first order in each reactant. It is a reversible process, which
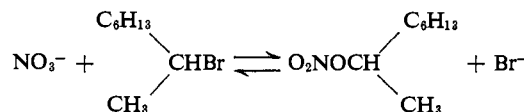
proceeds *without any detectable elimination*. The reaction is presumably a pure SN2 process moving towards an homogeneous equilibrium disturbed, however, by a side reaction in which bromide ions are removed from solution. The reaction of 2-octyl bromide with Et₄NNO₃ has a frequency factor of 10⁹·³ l. mole⁻¹ sec.⁻¹ and an activation energy, $E_a$, of 21.4 kcal. mole⁻¹.

</div>

**Table VIII.** Reaction of Alkyl Halides with $AgNO_3$ in $CH_3CN$

| Alkyl halide | $10^6 k_{2.5}{}^{44.6}$, l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$ | log $A$ | $E_a$, kcal. mole$^{-1}$ | % elim. at 44.6° | $\Delta(S_E - S_S)^a$ | $(E_E - E_S)^b$ |
|---|---|---|---|---|---|---|
| 1-Oct.Br | 1160 | 10.0 | 18.9 | 0.12 | $-0.8^c$ | $4.1^c$ |
| 2-Oct.Br | 3270 | 10.3 | 18.6 | 7.9 | $6.1^d$ | $3.5^d$ |
| 2-Oct.Cl | 7.0 | 11.1 | 23.7 | 3.3 | $5.6^c$ | $3.9^b$ |

$^a$ The term $\Delta(S_E - S_S)$ stands for the entropy increment for elimination over substitution. $^b$ The term $(E_E - E_S)$ stands for the energy increment of elimination over substitution. $^c$ For $[AgNO_3] = 0.080\ M$. $^d$ For $[AgNO_3] = 0.020\ M$.

The reaction of 2-octyl bromide with $AgNO_3$ has quite different kinetics to its reaction with $Et_4NNO_3$. 2-Octyl bromide, 1-octyl bromide, and 2-octyl chloride have all been found to exhibit the kinetic pattern $V = k_{2.5}[\text{alkyl halide}][AgNO_3]^{1.5}$ such that the 2.5-order rate coefficient, $k_{2.5}$, is a constant at a given temperature: for each alkyl halide the variation of this rate coefficient with temperature was found to obey the Arrhenius equation. For each of several runs throughout which the integrated 2.5-order rate coefficients were calculated good constancy was obtained up to at least 75% reaction. This indicates that under the normal conditions of our runs, mechanisms involving heterogeneous catalysis by AgBr do not contribute significantly to the over-all kinetics. For 2-octyl bromide direct evidence of the absence of heterogeneous catalysis by AgBr precipitated *during* the course of a run was independently obtained (Experimental Section). The reaction of 2-octyl bromide with $Et_4NNO_3$ occurred without elimination, but in the corresponding reaction with $AgNO_3$ elimination was an important component; the olefin proportion being constant throughout each run. The rate of reaction of 2-octyl bromide with $AgNO_3$ is far greater than the corresponding rate of reaction with $Et_4NNO_3$. Conductivity data shows that, although not identical, the extents of dissociation of $Et_4NNO_3$ and $AgNO_3$ are similar, and it follows consequently that the silver ion is intervening in the rate-determining step. At 44.6°, with the concentrations of 2-octyl bromide and of salt both 0.02 $M$, the ratio of initial rates of reaction is $V_{Et_4NO_3}:V_{AgNO_3} = 1:112$. A comparison of the reaction of $AgNO_3$ with various alkyl halides is given in Table VIII. Due mainly to a much greater Arrhenius energy parameter, the reaction of $AgNO_3$ with 2-octyl chloride is at a given temperature far slower than that with an equivalent concentration of 2-octyl bromide; irrespective of detailed mechanism, the carbon–halogen bond must be partially broken in the transition state and the ionic bond between $Ag^+$ and the departing halide ion partially made in the transition state. The carbon–chlorine bond is of considerably greater strength than a corresponding carbon–bromine bond and thus more than compensates the relative energies of interaction $Ag^+$ with $Cl^-$ and $Br^-$, respectively.

The main interest in a comparison of the reaction of silver nitrate with 2-octyl chloride and 2-octyl bromide lies however in the relative proportions of olefin produced with these two alkyl halides. It is readily seen that at all temperatures the ratio of elimination to substitution is higher for the bromide than for the chloride and this shows that the two reactions do not occur *via* a common intermediate such as a free carbonium ion (2-octyl cation) or even a carbonium

nitrate ion pair. *In particular it appears that in the product-forming step the departing halogen must still be in the sphere of influence of the carbon.* Insofar as there are strong arguments against these being concurrent $S_N2$–$Ag^+$ and $E2$–$Ag^+$ reactions and in favor of some type of ionization preceding both substitution and elimination, the contrast between the $AgNO_3$ reaction with 2-octyl chloride and bromide must be ascribed to the proximity of (encumbrance by) the counter halide ion in the product-determining step as shown.
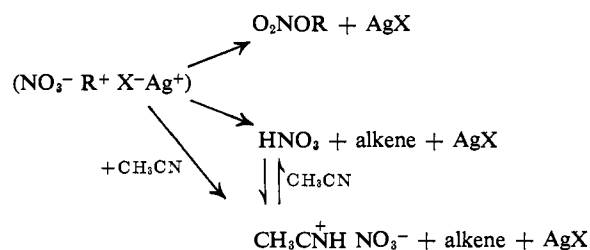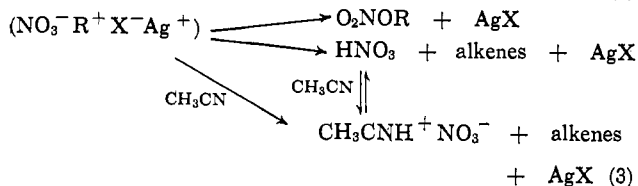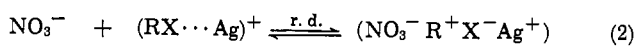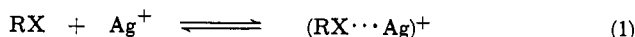
The structure of the carbonium nitrate silver halide ion quadruplet is not known in detail, but we were able to show that the substitution product under *kinetically controlled* conditions proceeds with almost complete inversion of optical configuration.[27]

In attempting to define the stoichiometric composition of the activated complex, the kinetic pattern which was obtained must be examined more closely. At the highest silver nitrate concentrations studied we are approaching conditions where the three-halves order could be explained in terms of a transition state incorporating one $Ag^+NO_3^-$ pair and either $Ag^+$ or $NO_3^-$. Since the reaction is half order[28] in the sum of stoichiometric $[AgNO_3]$ and $[Et_4NNO_3]$, the nitrate ion must be incorporated into the transition state. These observations are qualitatively consistent with a mechanism in which both paired and unpaired silver ions are equally effective electrophiles while only the free nitrate is an effective nucleophile (Scheme I).

(27) Y. Pocker and D. N. Kevill, to be published as part V in this series; see also N. Kornblum and D. E. Hardies, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956, p. 2-O.

(28) By using $AgNO_3$–$Et_4NNO_3$ mixtures, the concentration of silver ion and of nitrate ion can be varied independently, and we were able to show that the kinetic equation is of the form: $V = k_{2.5}[\text{2-Oct.Br}][AgNO_3]\{[AgNO_3] + [Et_4NNO_3]\}^{0.5}$ and that there is no change in the olefin proportion of the products. This constancy in the product ratio is a strong indication that no new mechanism is introduced but merely a speeding up of the reaction with $AgNO_3$ alone. It should also be noted that Donnan and Potts[5] and Burke and Donnan[6] investigated the kinetics of reaction of silver nitrate with EtI in $CH_3CN$ and with EtI and $n$-BuI in EtOH and found that their reaction is of a higher order than second. One can show using their data that the calculated 2.5-order coefficients are fairly constant; thus the reaction of EtI with $AgNO_3$ appears to be governed by $k_{2.5} = 8.5 \pm 0.4 \times 10^{-3}$ l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$, the reaction of $n$-BuI with $AgNO_3$ in EtOH, by $k_{2.5} = 4.8 \pm 0.5 \times 10^{-2}$ l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$, and the reaction of EtI with $AgNO_3$ in EtOH, by $k_{2.5} = 13.6 \pm 1.8 \times 10^{-2}$ l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$.

## Scheme I

$$RX + Ag^+ \rightleftharpoons (RX\cdots Ag)^+ \qquad (1)$$

$$NO_3^- + (RX\cdots Ag)^+ \xrightleftharpoons{r.\,d.} (NO_3^-R^+X^-Ag^+) \qquad (2)$$

$$(NO_3^-R^+X^-Ag^+) \longrightarrow O_2NOR + AgX$$
$$\searrow HNO_3 + alkenes + AgX$$

$$CH_3CN\searrow \qquad CH_3CN\Big\Vert$$

$$CH_3C\overset{+}{N}H\,NO_3^- + alkenes$$
$$+ AgX \qquad (3)$$

The symbol $Ag^+$ is used here to represent both free and paired silver ions irrespective of their state of solvation in acetonitrile. In step 3 it is difficult to assess whether the proton is removed by $CH_3CN$ influenced by $NO_3^-$ or whether it is removed directly by $NO_3^-$ itself. The latter represents the simpler interpretation; however, both descriptions are consistent with the observation that the ratio of elimination to substitution is essentially independent of $[NO_3^-]$.

The main difficulty in a more quantitative interpretation of these kinetics is that the 0.5 order in stoichiometric nitrate was obtained over a very wide range of concentrations. One way in which it is possible to accommodate all the observations is by assuming that the concentration of free nitrate ions which are *effective in the kinetic sense*[29] is smaller than that recorded by conductance.

The transition state theory leads to a similar conclusion. Accepting the stoichiometric composition of the activated complex as $(NO_3^-, RX, Ag^+)$, the ratio of activity coefficients of ground state *vs.* transition state, $f_{NO_3}\cdot f_{RX}f_{Ag^+}/f_*$, would be expected to be subject to a substantial negative salt effect which if proportional to the square root of the ionic strength would cause a reduction in the apparent order in nitrate from 1 to 0.5. Indeed, in the presence of large but constant amounts of $Et_4NClO_4$ the rate is reduced,[30] but the order in stoichiometric nitrate rises from 0.5 towards 1.

Silver ion catalyzed $S_N1$-like and $S_N2$-like reactions as formulated by Hughes and Ingold[31] can be considered as representing two extremes in the range of mechanisms in which differing degrees of electrophilic and nucleophilic assistance to reaction occur. When the nucleophilic assistance produces an ion pair $(NO_3^-R^+)$ or a quadruple ion $(NO_3^-R^+X^-Ag^+)$ we are dealing with an *anion-promoted ionization* which may lead to rearranged products (through the isomerization of the $R^+$ partner).

The results reported in the present investigation pertaining to the reaction of *sec*-alkyl halides with $AgNO_3$ in $CH_3CN$ are best explained in terms of a rate-determining step leading to an ion-quadruplet intermediate $(NO_3^-R^+X^-Ag^+)$. In this mechanism we visualize that one and the same $NO_3^-$ is involved in both the rate-determining step and in the product-determining step. In the nonhydroxylic solvent $CH_3CN$ the nitrate ion is sufficiently nucleophilic to preclude any solvent intervention and it follows from the above mechanism that although acceleration by added free $NO_3^-$ will occur, the product ratio will be a constant independent of $[NO_3^-]$ (see Scheme I).

## Experimental Section

*2-Octyl Bromide.* This compound was a B.D.H. product. It was purified by careful fractionation under reduced pressure through a 200-mm. glass helix column. A constant-boiling middle fraction was collected and refractionated, and the middle fraction was collected; $n^{25}D$ 1.4478 (lit.[32] $n^{25}D$ 1.4481).

*1-Octyl Bromide.* The B.D.H. product was purified in the same manner as was the 2-octyl bromide. After purification it showed $n^{25}D$ 1.4498 (lit.[33] $n^{25}D$ 1.4503).

*2-Octyl Chloride.* A purified and freshly distilled sample was kindly presented by Dr. W. A. Mueller; $n^{25}D$ 1.4248 (lit.[34] $n^{19.3}D$ 1.4270).

*Tetraethylammonium Nitrate.* The product from either of two methods of preparation gave identical kinetic results. (i) An aqueous solution of tetraethylammonium hydroxide (B.D.H.) was neutralized by slowly adding concentrated Analar grade nitric acid. The solution was then evaporated to dryness under reduced pressure on a water bath. The product was recrystallized from acetonitrile–ether and dried under vacuum. (ii) Tetraethylammonium bromide (B.D.H.) was dried for several hours at 120° and then reacted with the requisite amount of silver nitrate in acetonitrile solution. Samples were withdrawn from the reaction mixture and titrated potentiometrically. The concentrations were adjusted accordingly until *exact* equivalence was attained. The silver bromide was filtered off and the tetraethylammonium nitrate precipitated from solution by the addition of ether and recrystallized from acetonitrile–ether and dried under vacuum.

*Tetraethylammonium Bromide.* The B.D.H. product was dried for several hours at 120°, recrystallized from acetonitrile, and redried: $Br^-$, 37.9% (calcd. for $C_8H_{20}NBr$: $Br^-$, 38.0%).

*Tetraethylammonium Perchlorate.* An aqueous solution of tetraethylammonium hydroxide was neutralized by adding Analar 60% perchloric acid until neutral to litmus. The precipitated perchlorate was filtered, recrystallized from water, and dried under vacuum.

*Tetraethylammonium Nitrite.* Tetraethylammonium iodide was reacted with the requisite amount of silver nitrite (purified as indicated below) in acetonitrile solution. The methods used for its isolation and purification were similar to those described for the corresponding nitrate. The nitrite was analyzed by adding a weighed portion to an excess of a standard solution of ceric ammonium sulfate in 2 $N$ $H_2SO_4$ and back titrating against a ferrous ammonium sulfate solution, using N-phenylanthranilic acid as indicator: $NO_2^-$, 26.04% (calcd. for $C_8H_{20}NNO_2$: $NO_2^-$, 26.1%).

(29) In the absence of silver ions, nitrate ions react with 2-octyl bromide in $CH_3CN$ *via* an $S_N2$ process and the free and paired ions do not appear to differ significantly in their nucleophilicities. On the other hand, in the silver ion catalyzed process, the nitrate ion is attacking a positively charged complex (Scheme I, step 2); electrostatic factors will be of prime importance in determining the free energy of this process and the free nitrate ion would be expected to have a significantly greater nucleophilicity.

(30) The retardation produced by $Et_4NClO_4$ is consistent with the negative salt effect suggested above; it is however also consistent with the removal of free $NO_3^-$ by $Et_4N^+$ due to ion pairing.

(31) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 358.

(32) R. Letsinger, *J. Am. Chem. Soc.*, 70, 40 (1948).

(33) I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, London, 1953.

(34) E. J. Corey and W. J. Wechter, *J. Am. Chem. Soc.*, 76, 6040 (1954).

Table IX. Equivalent Conductances (ohm$^{-1}$ cm.$^2$ mole$^{-1}$) of Various Salts and Mixtures in CH$_3$CN at 25.0°

(i) [AgClO$_4$] = C

| $10^5C$ | 7.60 | 15.2 | 30.3 | 60.5 | 121 | 242 | 483 | 965 | 1930 | 3850 | 7700 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 203 | 202 | 197 | 196 | 194 | 189 | 162 | 158 | 154 | 132 | 116 | |

(ii) [AgNO$_3$] = C

| $10^5C$ | 7.74 | 15.5 | 31.0 | 62.1 | 124 | 248 | 497 | 994 | 1990 | 3980 | 7950 | 15,900 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 192 | 191 | 183 | 178 | 168 | 161 | 137 | 117 | 101 | 86 | 65 | 52 |

(iii) [AgNO$_2$] = C

| $10^5C$ | 3.73 | 7.45 | 14.9 | 29.8 | 59.4 | 119 | 239 | 477 | 954 | 1910 |
|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 49.9 | 39.6 | 34.2 | 28.6 | 26.1 | 23.9 | 22.2 | 21.9 | 21.3 | 21.3 |
| $10^5C$ | 3810 | 7600 | 15,600 | | | | | | | |
| Λ | 21.0 | 19.4 | 20.1 | | | | | | | |

(iv) [Et$_4$NClO$_4$] = C

| $10^5C$ | 6.25 | 12.5 | 24.9 | 49.8 | 99.5 | 199 | 398 | 795 | 1590 | 3180 | 6350 | 12,700 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 203 | 202 | 194 | 186 | 180 | 180 | 157 | 141 | 128 | 110 | 88 | 59 |

(v) [Et$_4$NNO$_3$] = C

| $10^5C$ | 3.88 | 7.75 | 31.0 | 62.1 | 124 | 132 | 248 | 497 | 994 | 1450 |
|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 197 | 194 | 194 | 182 | 178 | 182 | 173 | 156 | 141 | 134 |
| $10^5C$ | 1990 | 3980 | 7950 | 15,900 | | | | | | |
| Λ | 133 | 97 | 84 | 77 | | | | | | |

(vi) [Et$_4$NNO$_2$] = C

| $10^5C$ | 11.3 | 15.5 | 31.0 | 45.2 | 62.1 | 124 | 248 | 497 | 994 | 1990 |
|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 183 | 188 | 181 | 185 | 174 | 173 | 169 | 148 | 146 | 124 |
| $10^5C$ | 3980 | 7950 | 15,900 | | | | | | | |
| Λ | 104 | 88 | 84 | | | | | | | |

(vii) [AgNO$_3$] = C/2; [Et$_4$NNO$_3$] = C/2

| $10^5C$ | 3.88 | 7.75 | 15.5 | 31.0 | 62.1 | 124 | 248 | 497 | 994 | 1990 |
|---|---|---|---|---|---|---|---|---|---|---|
| Λ | 191 | 190 | 187 | 184 | 174 | 171 | 168 | 144 | 132 | 117 |
| $10^5C$ | 3980 | 7950 | 15900 | | | | | | | |
| Λ | 95 | 76 | 69 | | | | | | | |

(viii) [AgNO$_2$] = C; [Et$_4$NNO$_2$] = C

| $10^5C$ | 1.94 | 3.88 | 7.75 | 15.5 | 31.0 | 62.1 | 124 | 248 | 497 | 994 |
|---|---|---|---|---|---|---|---|---|---|---|
| Λ$^a$ | 201 | 189 | 187 | 186 | 179 | 172 | 167 | 162 | 145 | 138 |
| $10^5C$ | 1990 | 3980 | 7950 | | | | | | | |
| Λ$^a$ | 131 | 117 | 106 | | | | | | | |

$^a$ Assuming that the over-all concentration of electrolyte is $C$; if treated as in vii, it would have twice the quoted value.

*Silver Nitrate.* Analar grade silver nitrate was dried for several hours at 120°.

*Silver Nitrite.* A Johnson and Mathey product was carefully recrystallized from water, the temperature not being allowed to rise above 60° and crystallization being carried out in the dark. The yellow needles were filtered, washed with water, and allowed to dry (in the dark) under vacuum over concentrated H$_2$SO$_4$ for several days. Solutions of silver nitrite in CH$_3$CN were analyzed potentiometrically: Ag$^+$, 69.7% (calcd. for AgNO$_2$: Ag$^+$, 70.1%).

*Silver Perchlorate.* The B.D.H. product was dried at 120° for several hours and dissolved in dry benzene. The traces of water were azeotropically removed, and the solution was cooled and treated with dry pentane. The precipitated silver perchlorate was dried in a desiccator over P$_2$O$_5$ at 1 mm. for 24 hr. A weighed sample was analyzed by potentiometric titration: Ag$^+$, 53.3% (calcd. for AgClO$_4$: Ag$^+$, 53.2%).

*Solvent.* Acetonitrile was refluxed for 0.5 hr. over charcoal, a stream of nitrogen being passed. It was then filtered and dried over anhydrous potassium carbonate for 2 hr. After filtration, P$_2$O$_5$ was added and the acetonitrile was gently refluxed for 0.5 hr. before being decanted into a distillation flask and carefully distilled at atmospheric pressure using a 100 × 2 cm. (i.d.) column packed with glass helices. The first 200 and last 100 ml. of the distillate were discarded (acetonitrile forms an azeotrope with H$_2$O

and by discarding the first 200 ml. one obtains an essentially anhydrous distillate). The middle fraction, b.p. 80.3–80.5°, was chromatographed through freshly reactivated dry alumina (Al$_2$O$_3$ was dried at 200° under 0.1 mm. for 3 hr.) and carefully refractionated, the first and last 100 ml. of distillate being discarded. Starting with 4 l. of CH$_3$CN one obtains a 60–65% yield of pure solvent. The water content of acetonitrile was determined by titrating a weighed portion of the solvent in pure MeOH with Karl Fischer reagent. In various batches the water content did not exceed 0.4 m$M$ (1 m$M$ H$_2$O corresponds to 0.0018%). The specific conductance varied between 2 and 4 × 10$^{-8}$ ohm$^{-1}$ cm.$^{-1}$, $n^{25}$D 1.3417.

*Conductance Measurements at 25.0°.* From the measured resistances (accurate to 0.05%) of a salt or equimolar mixtures of salts at several concentrations and the known cell constant, the specific conductance, $\kappa$ (in ohm$^{-1}$ cm.$^{-1}$), of each of those solutions was obtained. After due correction for the specific conductance of the solvent, $\kappa_{CH_3CN} = 2 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$, the equivalent conductance, Λ (in ohm$^{-1}$ cm.$^2$ mole$^{-1}$) of the solution of the salt or equimolar mixture of salts at each particular concentration $C$ (mole l.$^{-1}$) was calculated from the formula Λ = 1000 ($\kappa - \kappa_{CH_3CN}$)/$C$. Two sets of measurements called series A and B were made at different times with different materials leading to essentially identical Onsager plots; the results obtained in series A are given in Table IX.

*Kinetic Techniques.* All the runs reported in this paper were carried out by the sealed bulb technique using 5.55-ml. aliquots of reaction mixture. The sealed bulbs were derived from 5 × 5/8 in. Monax test tubes, which were constricted, filled with the reaction mixture, and stoppered, and the contents were frozen in Dry Ice–alcohol mixture and then sealed. Five minutes with shaking was the time usually allowed for the tubes to come to temperature equilibrium with the bath after immersion. The tubes were removed at suitable intervals and stored in Dry Ice–alcohol mixture until opened and analyzed. Runs in which halide ions were produced in the absence of silver salts were followed by potentiometric titration in 40 ml. of acetone (containing 1 ml. of 1 *N* nitric acid and cooled in Dry Ice–alcohol) against standard aqueous silver nitrate solution using a silver wire electrode and a potassium nitrate–agar bridge to a dip-type calomel reference electrode. Runs in which the alkyl halides were reacted with silver salts were followed by a similar technique except that the samples were titrated against standard aqueous potassium chloride solutions. In the reaction of alkyl halides with silver nitrate it was found that the kinetics were of nonintegral order and the initial velocities $V_1 = (\Delta[Ag^+]/\Delta t)_1$ were obtained by calculating integrated, first-order rate coefficients with respect to silver nitrate throughout the runs, $k_1^{Ag^+}$ where $k_1^{Ag^+} = (2.303/t) \log a/(a - x)$ where $t$ is the reaction time in seconds, $a$ is the concentration of silver salt at the time zero, and $x$ is the concentration of silver nitrate consumed in time $t$. These integrated first-order rate coefficients were then plotted against $x$ and the plot was extrapolated to kinetic zero, due allowance being made for any small amount of reaction which occurred before the "initial" time zero. From the initial value for the first-order rate coefficient with respect to silver salt, the value for the *initial velocity*, $V_1$ (in l.$^{-1}$ mole sec.$^{-1}$) of the reaction was calculated. The various rate coefficients, $k_2^1$, $k_{2.5}^1$, and $k_3^1$ were then evaluated.

$$\frac{1}{[AgNO_3]}\left(\frac{-d[Ag^+]}{dt}\right) = k_1^{Ag^+}$$

$$k_1^{Ag^+}[AgNO_3] = V_1$$

$$V_1/[RX]_1 = k_1^1$$

$$V_1/[RX]_1[AgNO_3]_1 = k_2^1$$

$$V_1/[RX]_1[AgNO_3]_1^{1.5} = k_{2.5}^1$$

$$V_1/[RX]_1[AgNO_3]_1^2 = k_3$$

Since it was shown that the initial velocity of the reaction, $V^1_{AgNO_3}$, was governed by the equation $V^1_{AgNO_3} = k_{2.5}^1$[alkyl halide][silver nitrate]$^{1.5}$, we deduced equations for testing the constancy in the 2.5 order throughout each run. Let $a$ be the initial concentration of alkyl halide, and $b$ the initial concentration of $AgNO_3$; at any time ($t$) let $x$ moles of silver halide be formed, then $dx/dt = k_{2.5} (a - x)^{1.5}(b - x)$.

Integrating, we obtain for $a = b$

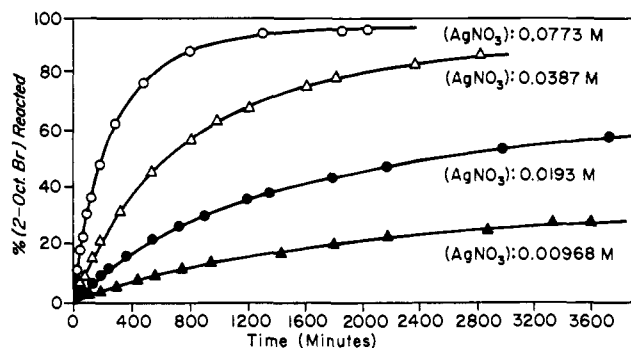$$k_{2.5} = \left[\frac{2}{3t}\frac{1}{(a - x)^{1.5}} - \frac{1}{a^{1.5}}\right]$$



Figure 4. The rates of AgBr production in the reaction of 2-octyl bromide (0.0193 *M*) with $AgNO_3$ in $CH_3CN$ at 44.6°.

for $a > b$

$$k_{2.5} = \frac{2}{(a - b)t}\left\{\frac{1}{\sqrt{a}} - \frac{1}{\sqrt{a - x}} + \frac{1}{2\sqrt{a - b}} \times \right.$$
$$\left. \ln\frac{\sqrt{a} - \sqrt{a - b}}{\sqrt{a} + \sqrt{a - b}} - \frac{1}{2\sqrt{a - b}}\ln\frac{\sqrt{a - x} - \sqrt{a - b}}{\sqrt{a - x} + \sqrt{a - b}}\right\}$$

for $a < b$

$$k_{2.5} = \frac{2}{(b - a)t}\left\{\frac{1}{\sqrt{a - x}} - \frac{1}{\sqrt{a}} + \frac{1}{\sqrt{b - a}} \times \right.$$
$$\left. \tan^{-1}\frac{\sqrt{a - x}}{\sqrt{b - a}} - \frac{1}{\sqrt{b - a}}\tan^{-1}\frac{\sqrt{a}}{\sqrt{b - a}}\right\}$$

The values obtained for the 2.5-order rate coefficients have been found to be constant *throughout each run*, indicating that the silver bromide precipitated as a consequence of the reaction cannot have any marked catalytic activity (Table X; *cf.* also Figure 4).

*Acid Formation.* The extent of acid formation was determined by titrating the aliquot against a standard methanolic solution of sodium methoxide. The titration was carried out in 30 ml. of acetone, previously rendered neutral to lacmoid indicator and cooled in a Dry Ice–alcohol mixture. When silver salts were present, this technique was modified so as to avoid any interference by silver ions during the titration. Prior to titration a solution of lithium chloride in acetone, rendered neutral to lacmoid, was added in excess of the amount required to precipitate all the silver as silver halide. In this way a clear solution was obtained and the titration was carried out conveniently. In several runs the extent of acid formation was determined at identical time intervals as the over-all reaction, and in this way a value for the ratio of elimination to over-all reaction could be obtained for each individual determination. In instances in which different time intervals were used for determining acid and silver bromide production the comparison was done graphically and read off for any required extent of reaction.

*Products.* Products were not isolated but published examples[35] show that both 1-octyl and 2-octyl halides react with $AgNO_3$ in $CH_3CN$ to give high yields of the corresponding octyl nitrates. The products from the reaction of 2-octyl bromide and $AgNO_3$ at 100°

(35) A. F. Ferris, K. J. McLean, I. C. Marks, and W. D. Emmons, *J. Am. Chem. Soc.*, 75, 4078 (1953).

Table X. Integrated 2.5-Order Rate Coefficients for the Formation of Silver Bromide[a]

| (A) At 44.6°: [AgNO₃] 0.0193 $M$, [2-Oct.Br] 0.0193 $M$ | | | | | | |
|---|---|---|---|---|---|---|
| Time, min. | 60 | 124 | 184 | 240 | 360 | 540 | 720 |
| % reaction | 3.5 | 6.5 | 9.4 | 11.7 | 16.0 | 21.8 | 26.4 |
| $10^3 k_{2.5}$ | 3.52 | 3.48 | 3.56 | 3.56 | 3.52 | 3.55 | 3.50 |
| Time, min. | 900 | 1200 | 1356 | 1780 | 2167 | 2963 | 3724 |
| % reaction | 30.5 | 35.9 | 38.7 | 44.2 | 48.4 | 54.7 | 59.3 |
| $10^3 k_{2.5}$ | 3.49 | 3.45 | 3.51 | 3.47 | 3.49 | 3.48 | 3.50 |

| (B) At 44.6°: [AgNO₃] 0.0387 $M$, [2-Oct.Br] 0.0193 $M$ | | | | | | |
|---|---|---|---|---|---|---|
| Time, min. | 21 | 42 | 60 | 120 | 180 | 310 | 521 |
| % reaction | 3.9 | 6.7 | 9.1 | 16.0 | 21.7 | 32.0 | 46.0 |
| $10^3 k_{2.5}$ | 3.18 | 3.25 | 3.36 | 3.22 | 3.15 | 3.04 | 3.48 |
| Time, min. | 814 | 994 | 1210 | 1610 | 1814 | 2369 | 2820 |
| % reaction | 57.4 | 63.5 | 68.6 | 75.6 | 79.1 | 84.0 | 87.0 |
| $10^3 k_{2.5}$ | 3.28 | 3.04 | 3.02 | 2.93 | 3.75 | 2.82 | 2.78 |

| (C) At 44.6°: [AgNO₃] 0.0193 $M$, [2-Oct.Br] 0.0387 $M$ | | | | | | |
|---|---|---|---|---|---|---|
| Time, min. | 30 | 63 | 102 | 148 | 221 | 360 | 480 |
| % reaction | 4.9 | 7.7 | 11.3 | 15.3 | 20.3 | 29.1 | 35.0 |
| $10^3 k_{2.5}$ | 3.44 | 3.23 | 3.28 | 3.38 | 3.26 | 3.34 | 3.32 |
| Time, min. | 746 | 935 | 1158 | 1636 | 2251 | 2702 | |
| %, reaction | 45.3 | 51.2 | 56.5 | 64.7 | 72.0 | 75.8 | |
| $10^3 k_{2.5}$ | 3.21 | 3.30 | 3.30 | 3.25 | 3.21 | 3.20 | |

[a] $k_{2.5}$ (l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$) calculated for various percentages of total possible stoichiometric reaction of 2-octyl bromide with AgNO₃ in CH₃CN.

were subjected to a gas chromatographic analysis; in addition to the solvent peak two major peaks and one very minor peak were obtained. By using synthetic samples we were able to identify[36] the reaction products as a mixture consisting of 2-octyl nitrate (~82%), cis- and trans-2-octene (~14%), and 1-octene (~2%).

*The Extent of Heterogeneous Catalysis by Silver Bromide.* Insofar as initial $k_{2.5}$ coefficients are in numerical agreement with integrated 2.5-order rate coefficients, the AgBr produced has no catalytic effect on the reaction under investigation. The absence of any autocatalysis due to silver bromide precipitated during the course of the reaction has been confirmed by taking a solution initially 0.0387 $M$ in both 2-octyl bromide and in silver nitrate and demonstrating that when the half-life time is superimposed upon the time zero of a plot of the extent of reaction against time for a solution initially 0.0193 $M$ in both reactants, then the two curves exactly coincide.

It was further shown that, when the concentration of each reactant was 0.0387 $M$, a plot of the extent of reaction against time was independent of whether the reaction tubes were protected from light by means of aluminum foil, or whether no precautions against irradiation by light were taken. This shows that the

(36) We are indebted to Messrs. J. W. Long and E. J. Campbell for their skillful assistance with this analysis.

observed absence of catalytic activity in the silver bromide precipitated during the course of reaction was not caused by the access of light to the reaction tubes. Since the above methods failed to detect any contribution to the rate due to AgBr precipitated during the reaction, we were interested to test the effect of externally prepared AgBr. To each reaction tube containing 5.55-ml. aliquots of a solution of 0.0200 $M$ in both silver nitrate and in 2-octyl bromide, 0.0200 g. of silver bromide was added, this being the weight required to make the silver bromide present equivalent to 0.0200 mole/l. of solution at 20.0°, if soluble (at 44.6° these correspond to 0.0193 $M$). The silver bromide used in this investigation was prepared by the reaction in the dark of concentrated solutions of 2-octyl bromide and silver nitrate in acetonitrile. The precipitate was filtered and washed with acetonitrile, methanol, and ether before drying in the dark, under vacuum over concentrated sulfuric acid. It was found that rates obtained with this silver bromide were essentially the same as those obtained in the absence of extraneously added silver bromide.