Electrophilic Catalysis in Nucleophilic Substitution and Elimination. IV. Kinetics of Reaction of 2-Octyl Bromide with Tetraethylammonium and Silver Perchlorates and Nitrites in Acetonitrile[1,2]

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The reaction of 2-octyl bromide with $AgClO_4$ in CH_3CN is first order in alkyl bromide, but the order in $AgClO_4$ rises quite continuously from unity, at very low [$AgClO_4$], to just over two at [$AgClO_4$] = 0.3 M. This behavior is analyzed in terms of a silver ion assisted ionization, which is nucleophilically promoted by CH_3CN and ClO_4^-. The reaction of 2-octyl bromide with Et_4N-NO_2 appears to be an S_N2 process, while the reaction of 2-octyl bromide with $AgNO_2$ is complex. It is of 2.5 order (first order in alkyl bromide and 1.5 order in $AgNO_2$), the rate of attack by $AgNO_2$ being slower than that by an equivalent concentration of Et_4NNO_2. Account being taken of the conductance measurements presented in the preceding paper a mechanistic pattern is developed involving electrophilic catalysis by both free and paired silver ions, with free NO_2^- acting in a nucleophilic capacity. The effect of added Et_4NNO_2 on the kinetics of reaction with $AgNO_2$ is shown to be in accord with the complex dissociation pattern of $AgNO_2$.

Introduction

For the more detailed study of electrophilic catalysis by Ag^+ it is advantageous to vary the nucleophilic capacity of the anion while retaining the same substrate and solvent. Whereas in the preceding paper[1] the NO_3^- ion played the role of a fairly good nucleophile capable of intervening in the rate-determining step of the Ag^+-assisted reaction, in the present paper the kinetic study is directed toward both extremes. On the one hand $AgClO_4$ is used, *i.e.*, the silver salt employed contains the weakly nucleophilic anion ClO_4^-; and on the other hand $AgNO_2$ is used, *i.e.*, the silver salt employed formally contains the strong nucleophile NO_2^-. Redies and Iredale[4] have studied the kinetics of reaction between $AgClO_4$ and CH_3I in benzene and found the reaction to be of over-all order of 2.5. It is possible to infer from the data quoted that the 2.5 order is made up as follows[5,6]: $V = k_{2.5}[CH_3I]^{1.0}[AgClO_4]^{1.5}$.

Hammond, Hawthorne, Waters, and Graybill[7] have studied the reactions of $AgClO_4$ with isopropyl and neopentyl iodides in acetonitrile and with methyl iodide in acetone and found that in acetone over the limited range studied the reactions become third order after a correction was made for the large degree of association of $AgClO_4$ in that solvent. The catalytic effect of added $LiClO_4$ led them to suggest that the ClO_4^- ion is included in the rate-determining step. This suggestion is in substantial agreement with that made earlier by Kornblum[8] who found neopentyl iodide to be relatively unreactive with respect to $AgNO_2$. Kornblum, *et al.*,[9] have also shown that the reaction of $AgNO_2$ with 2-octyl bromide in ether yields 2-octyl nitrite and 2-nitrooctane by inversion with essentially complete retention of optical purity.

When the anionic reagent is sufficiently reactive, nucleophilic solvent intervention by CH_3CN is low.[1,7,8,10] However when the anionic reagent is inherently a weak nucleophile or is sterically precluded from reacting with R^+ or if it reversibly reacts with R^+ to produce an easily ionizable ester or onium salt, then products derived from the alkylation of CH_3CN by R^+ are known to arise.[11-15]

Results

1. Effect of Added Et_4NClO_4 on the Stability of 2-Octyl Bromide in CH_3CN. The production of Br^- from 2-octyl bromide in CH_3CN at 100.1° is slow; for instance after 14 hr., less than 1% of the bromine from a 0.160 M solution exists as Br^-. When varying concentrations of Et_4NClO_4 are added to a constant concentration of 2-octyl bromide (Table I), a *nonlinear* increase in the initial first-order rate coefficient for the production of Br^- is observed (Figure 1).

In the presence of Et_4NClO_4 the olefin proportion of the products falls as the reaction proceeds, presumably a side reaction removes olefin after it has been formed. This side reaction apparently involves ClO_4^-, since it did not occur in the absence of added Et_4NClO_4. The *initial* olefin proportion of products in the presence

(1) Part III: Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, 87, 4760 (1965).
(2) Taken from part of the thesis presented by Dennis N. Kevill in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of London, Jan. 1960.
(3) To whom inquiries should be directed. Department of Chemistry, University of Washington, Seattle, Wash. 98105.
(4) M. F. Redies and T. Iredale, *J. Phys. Chem.*, 48, 224 (1944).
(5) The reaction products are a mixture of methyl perchlorate[4] and a little toluene: H. Burton and P. F. G. Praill, *Chem. Ind.* (London), 939 (1951).
(6) Benzyl and benzhydryl perchlorates also alkylate benzene but triphenylmethyl perchlorate is stable in benzene: H. Burton and G. W. H. Cheeseman, *J. Chem. Soc.*, 832 (1953).

(7) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Am. Chem. Soc.*, 82, 704 (1960).
(8) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *ibid.*, 77, 6269 (1955).
(9) N. Kornblum, L. Fishbein, and R. A. Smiley, *ibid.*, 77, 6261 (1955).
(10) A. F. Diaz and S. Winstein, *ibid.*, 86, 5011 (1964).
(11) J. J. Ritter and P. Minieir, *ibid.*, 70, 4045 (1948).
(12) J. Cast and T. S. Stevens, *J. Chem. Soc.*, 4180 (1953); the isolated product is N-benzhydrylacetamide.
(13) G. W. H. Cheeseman, *Chem. Ind.* (London), 281 (1954); S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, 76, 4468 (1954).
(14) Y. Pocker and D. W. Hills, unpublished observations.
(15) N. Kornblum, *et al.*,[8] refer to B. Taub, Ph.D. Thesis, Purdue University, June 1952.
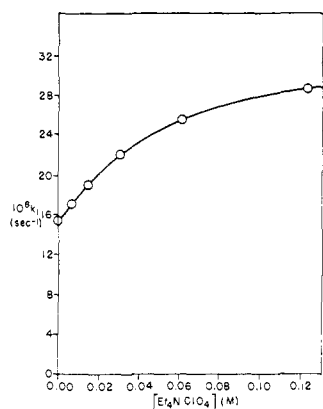
Figure 1. Effect of added Et_4NClO_4 on the initial first-order rate coefficient for the production of bromide ions from 2-octyl bromide (0.0800 M) in CH_3CN at 100.1° (concentration quoted at 20°).

of Et_4NClO_4 as obtained by extrapolation to time zero is 85%, a value which within the experimental error is identical with 84%, the value obtained in the absence of Et_4NClO_4.[1] The substitution product is apparently N-alkylated acetonitrile.

Table I. The Solvolysis of 2-Octyl Bromide by CH_3CN at 100.1°[a]

$[Et_4NClO_4]$, M	$10^7 k_1^i$, sec.$^{-1a}$
0.000	15.4
0.00775	17.1
0.0155	19.1
0.0310	22.1
0.0620	25.3
0.124	28.4

[a] Each individual run shows a marked autocatalysis; k_1^i was obtained by extrapolation of [Br$^-$] to zero. [2-Oct Br] = 0.080 M.

2. The Reaction of Silver Perchlorate and 2-Octyl Bromide in CH_3CN.

Silver perchlorate reacts with 2-octyl bromide at 60.0° with measurable speed, and the kinetics have been thoroughly investigated at this temperature and also over a more limited range at 44.6,

Table II. Initial Second-Order Rate Coefficients for AgBr Production in the Reaction of 2-Octyl Bromide with $AgClO_4$ in CH_3CN

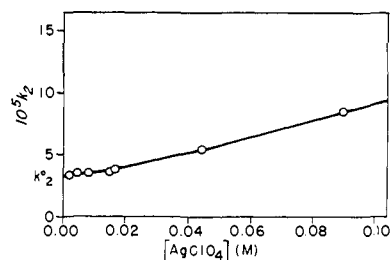| Temp., °C.	[2-Oct.Br]	$[AgClO_4]$	$10^5 k_2$
44.6	0.0378	0.0155	0.578
	0.0378	0.0310	0.715
60.0	0.0095	0.0164	4.06
	0.0189	0.0164	4.18
	0.0378	0.00206	3.39
	0.0378	0.00412	3.56
	0.0378	0.00824	3.57
	0.0378	0.0151	3.69
	0.0378	0.0164	3.85
	0.0378	0.0447	5.41
	0.0378	0.0893	8.32
	0.0756	0.146	14.9
	0.0378	0.179	15.6
	0.151	0.292	26.7
90.5	0.0378	0.0155	80
	0.0378	0.0310	93
100.1	0.0378	0.00436	170
	0.0378	0.00872	192
	0.0378	0.0174	219
	0.0378	0.0348	248

Figure 2. Extrapolation of second-order rate coefficients k_2 (l. mole^{-1} sec.$^{-1}$) to obtain k_2^0 for the reaction of 2-octyl bromide with $AgClO_4$ in CH_3CN at 60.0°.

90.5, and 100.1° (Table II). At any given temperature the reaction goes more slowly than the corresponding reaction with silver nitrate. Second-order integrated rate coefficients were calculated throughout each run according to the equation

$$\frac{d[AgBr]}{dt} = k_2[\text{2-Oct.Br}][AgClO_4]$$

At 60.0°, it was formally shown that the order in 2-octyl bromide was unity, but *the order in silver perchlorate was shown to increase as the concentration of silver perchlorate is increased* (Figure 2). At low concentrations (around 0.002 M) the order in silver perchlorate approaches a limiting value of unity; at higher concentrations the order rises continuously, until with 0.3 M silver perchlorate the order is just greater than 2. For the lower concentrations of silver perchlorate, the integrated second-order rate coefficients (k_2) were found to be sensibly constant throughout each run, and the initial value for the coefficient was identical with its mean value. For higher concentrations of silver perchlorate the integrated second-order coefficients fell off in value as the run progressed and strictly initial values for the coefficient were obtained by extrapolation. From the initial values for the second-order coefficients (k_2), the initial values for the first-order coefficient (k_1) with respect to 2-octyl bromide can be obtained. A plot of log k_1 vs. log C, where C is the concentration of silver perchlorate, is such that the slope at any point gives the order in silver perchlorate for the concentration involved (Figure 3). A brief investigation has also been made at 44.6, 90.5, and 100.1° with the concentration of silver perchlorate being varied between 0.004–0.04 M. The *formal order* in silver perchlorate over this limited range is sensibly constant at 1.2; this behavior is identical with that observed at 60.0°. While mixed-order kinetics are in general observed, it is possible to isolate by extrapolation the limiting component of reaction which is strictly first order in stoichiometric silver perchlorate. Presumably in this limiting case the clean second-order kinetics are due to the isolation of a single reaction path. Values of k_2^0 (l. mole^{-1} sec.$^{-1}$) obtained by the extrapolation of initial second-order coefficients to zero silver perchlorate concentration for various temperatures are given below.

Temp., °C.	44.6	60.0	90.5	100.1
$10^5 k_2^0$	4.4	31	670	1500

The Arrhenius plot of this rate data (Figure 4) leads to values for the activation energy of 24.5 kcal. mole^{-1} and for the frequency factor of $10^{11.5}$ l. mole^{-1} sec.$^{-1}$.
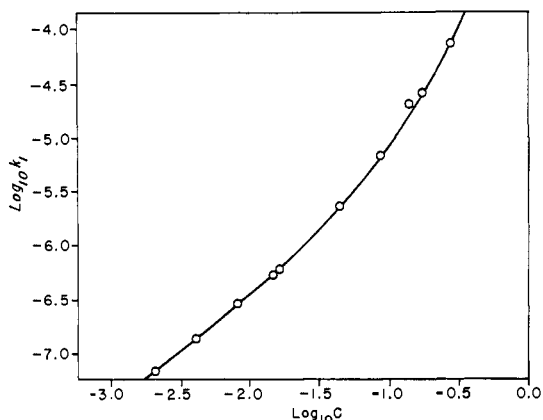
Figure 3. First-order rate coefficients for the reaction of 2-octyl bromide with AgClO₄ in CH₃CN at 60.0°, plotted logarithmically against the concentration of AgClO₄.

Figure 4. Arrhenius plot of the limiting second-order rate coefficient, k_2^0 (l. mole^{-1} sec.$^{-1}$), for the reaction of 2-octyl bromide with AgClO₄ in CH₃CN.

Added tetraethylammonium perchlorate accelerates the reaction. Two series of runs have been carried out: in each tetraethylammonium perchlorate was added to a constant concentration of 2-octyl bromide and silver perchlorate. In the first series a relatively low concentration of silver perchlorate was chosen (0.0151 M). The second-order coefficients (k_2) for any given run were sensibly constant, but they increased from run to run as the concentration of added tetraethylammonium perchlorate increased. For this series the initial velocity (V_i) could be *formally* expressed by the equation $V_i = k_{2.20}[2\text{-Oct}.\text{Br}][\text{AgClO}_4]\{[\text{AgClO}_4] + [\text{NEt}_4\text{ClO}_4]\}^{0.20}$ where $k_{2.20}$ was a constant (Table III).

Table III. Effect of Added Et₄NClO₄ on the Reaction between AgClO₄ and 2-Octyl Bromide in CH₃CN at 60.0°

(a) [AgClO₄] = 0.0151 M; [2-Oct.Br] = 0.0378 M

[Et₄NClO₄], M	$10^5 k_2$, l. mole^{-1} sec.$^{-1}$	$10^5 k_{2.2}$, l.$^{1.2}$ mole$^{-1.2}$ sec.$^{-1}$
0.000	3.69	8.5
0.0146	4.40	8.4
0.0293	4.84	8.5
0.0586	5.09	8.5
0.117	6.13	9.1

(b) [AgClO₄] = 0.146 M; [2-Oct.Br] = 0.0756 M

[Et₄NClO₄], M	$10^5 k_2$, l. mole^{-1} sec.$^{-1}$	$10^4 k_{2.5}$, l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$
0.000	14.9	3.9
0.117	19.7	3.9
0.240	25.2	4.0

The second series of runs was carried out with a tenfold higher concentration of silver perchlorate (0.146 M). In this region the reaction order could be formally expressed by the equation $V_i = k_{2.5}[2\text{-Oct}.\text{Br}]\cdot[\text{AgClO}_4]\{[\text{AgClO}_4] + [\text{Et}_4\text{NClO}_4]\}^{0.50}$.

Titration in acetone against sodium methoxide yields values for the acid concentration corresponding to almost the entire extent of over-all reaction. Elimination can, however, be conveniently estimated by a
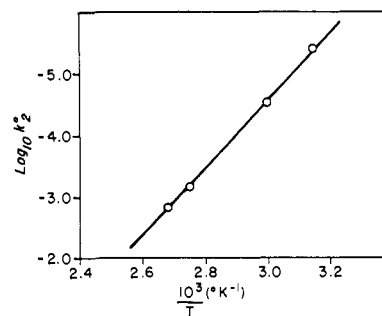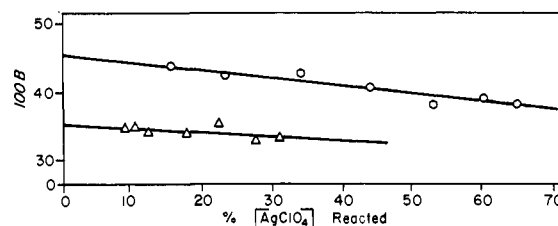

Figure 5. The decrease in the proportion of olefinic products during the course of the reaction of 2-octyl bromide with AgClO₄ (0.0174 M) in CH₃CN: O, [RBr] = 0.0226 M, kinetics run at 100.1°; △, [RBr] = 0.0400 M, kinetics run at 60.0° (concentrations quoted for 20°).

method involving direct bromine addition to the olefin. The proportion of elimination (B) decreases as the re-

$$B = \frac{\text{moles of olefin present}}{\text{moles of 2-octyl bromide reacted}}$$

action progresses, an effect which is also observed when silver perchlorate alone reacts with the 2-octyl bromide. The decrease appears to be a linear function of the over-all extent of reaction. Olefins in the presence of acids react with nitriles.[5,6] The isolated products are amides, formed by the facile hydrolysis of the initially formed acetonitrilium salt. The octenes produced during the elimination process are accompanied by concurrent perchloric acid production; the carbonium ions arising from the interaction of perchloric acid with olefins may either lose a proton to regenerate olefin, or alternatively they can N-alkylate the solvent molecule, with loss of initially formed olefin. In order to avoid these slow side reactions, the initial proportion of elimination, B^0, was obtained by a linear extrapolation of B to zero reaction (Figure 5). Consequently, B^0 represents the way in which the stable reaction products are initially partitioned between substitution ($1 - B^0$) and elimination (B^0).

The value of B^0 increased somewhat as the over-all concentration of silver perchlorate increased (Figure 6). The rate of increase of B^0 with initial silver perchlorate concentration is small enough for it to be considered as due to a differential salt effect in the partitioning process between elimination and substitution (a similar effect was observed in the reaction between 2-octyl bromide and silver nitrate in acetonitrile). The relevant data are given in Table IV. With a concentration of silver perchlorate of 0.0174 M and of 2-octyl bromide of 0.0226 M, it was found that a run
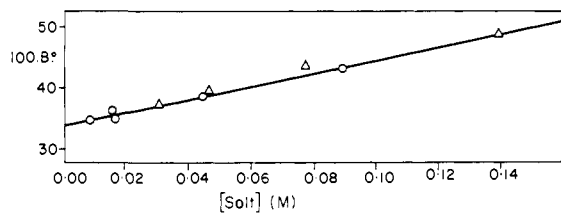
Figure 6. Effect of perchlorate salt concentration on the initial proportion of olefinic products in the reaction 2-octyl bromide with $AgClO_4$ in CH_3CN at 60.0°: O, $AgClO_4$; △, $AgClO_4$ (0.0151 M) + Et_4NClO_4.
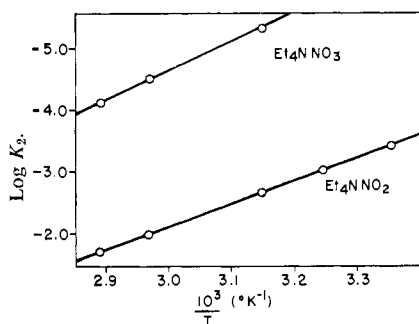

Figure 7. Arrhenius plots for the reaction of 2-octyl bromide with Et_4NNO_3 and Et_4NNO_2 in CH_3CN.

at 100.1° led to an initial value for the olefin proportion of 45.8%, showing that elimination is favored relative to substitution by a rise in temperature.

Table IV. Values for the Ratio B^0 of Moles of Olefin Produced Relative to Moles of 2-Octyl Bromide[a]

(a) [2-Oct.Br] = 0.0378 M		(b) [2-Oct.Br] = 0.0378 M; [$AgClO_4$] = 0.0151 M	
[$AgClO_4$], M	100 $B°$	[Et_4NClO_4], M	100 $B°$
0.00824	34.9	0.0000	36.2
0.0151	36.2	0.0146	37.3
0.0164	35.1	0.0293	39.6
0.0447	38.8	0.0586	43.8
0.0893	43.0	0.117	48.8

[a] Reacted in the initial stages of reaction in CH_3CN at 60.0°. Expressed as a function of the concentration of (a) $AgClO_4$ and of (b) Et_4NClO_4.

3. Reaction of Et_4NNO_2 with 2-Octyl Bromide in CH_3CN. Only the over-all rate of reaction has been measured, *i.e.*, the rate of production of bromide ions. The integrated second-order coefficients for up to at least 40% of stoichiometrically possible reaction are sensibly constant (Table V). In contrast to the SN2 process involving NO_3^-, equilibrium is essentially never established. After several hours a side reaction (probably several side reactions) becomes important, and the solution adopts a yellow color. Eventually the bromide ion concentration reaches a maximum and then decreases.[16] The variation of the second-order rate coefficients with temperature, expressed in conventional Arrhenius plots, are contrasted with those

(16) Similar complications have been previously encountered in the reaction of *t*-BuBr with Et_4NNO_2 in nitromethane: P. B. D. de la Mare, E. D. Hughes, C. K. Ingold, and Y. Pocker, *J. Chem. Soc.*, 2930 (1954); for analogous complications in dimethylformamide see N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Moobery, E. P. Oliveto, and G. E. Graham, *J. Am. Chem. Soc.*, 78, 1497 (1956).
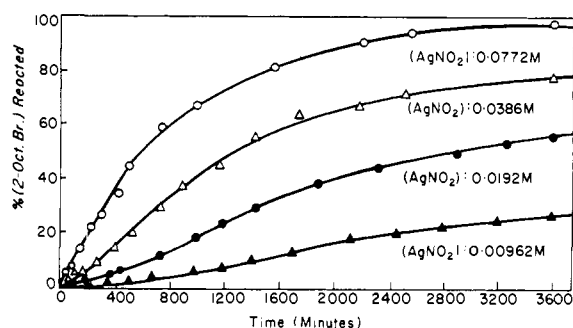

Figure 8. Rates of AgBr production in the reaction of 2-octyl bromide (0.0193 M) and $AgNO_2$ in CH_3CN at 44.6°.

for the corresponding reaction with Et_4NNO_3 (Figure 7).

4. Reaction of $AgNO_2$ with 2-Octyl Bromide in CH_3CN. The over-all rate of reaction has been studied at 44.6° (Figure 8). At this temperature the reaction is slower than reaction of the 2-octyl bromide with an equivalent concentration of silver nitrate and also much slower than reaction with an equivalent concentration of tetraethylammonium nitrite.

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

Temp., °C.	[Et_4NNO_2], M	[2-Oct.Br], M	10^3k_2
25.0	0.0372	0.0199	0.364
35.0	0.0183	0.0392	0.96
44.6	0.0180	0.00966	2.17
44.6	0.0180	0.0387	2.06
44.6	0.0180	0.0193	2.14
44.6	0.0360	0.0193	2.10
44.6	0.0277	0.0193	2.22
44.6	0.0138	0.0193	2.26
44.6	0.00910	0.0193	2.19
44.6	0.00452	0.0193	2.17
63.8	0.00878	0.0187	10.4
72.9	0.0169	0.00902	19.9

[a] k_2 (l. mole^{-1} sec.$^{-1}$) for the production of bromide ions in the reaction of 2-octyl bromide with Et_4NNO_2 in CH_3CN at various temperatures. $k_2 = Ae^{-E_a/RT}$; $A = 10^{9.1}$ l. mole^{-1} sec.$^{-1}$, $E_a = 17.2$ kcal. mole^{-1}.

Conductance data shows[1] that silver nitrite is only partly dissociated and that the ions present are not those resulting from a simple dissociation, but are almost certainly composed of Ag^+ and $Ag(NO_2)_2^-$ with only very few free NO_2^- ions. Compared to NO_2^- the $Ag(NO_2)_2^-$ ions do not appear to have a high nucleophilicity. The initial velocity (V_i) of the reaction can be expressed over *the whole concentration range* investigated by the equation $V_i = k_{2.5}$[2-Oct.Br][$AgNO_2$]$^{1.5}$ such that the 2.5-order rate coefficient, $k_{2.5}$, is a constant (Table VI).

To a constant concentration of silver nitrite and of 2-octyl bromide at 44.6°, various concentrations of tetraethylammonium nitrite were added (Table VII). When the concentration of added tetraethylammonium nitrite was smaller than that of silver nitrite, the increase in rate was surprisingly small, being far smaller than one would expect for an SN2 process involving 2-octyl bromide and tetraethylammonium nitrite. When the concentrations of added tetraethylammonium nitrite exceeded those of silver nitrite, there was a

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

[AgNO$_2$], M	[2-Oct.Br], M	Initial velocity (V_i), $10^8 V_i$	$10^4 k_{2.5}$
0.0193	0.00966	1.54	6.0
0.0193	0.0194	3.3	6.4
0.0193	0.0387	6.7	6.9
0.0193	0.0773	14.5	7.0
0.00968	0.0773	5.9	8.1
0.3086	0.0773	42.5	7.2
0.0771	0.0773	114	6.9
0.00962	0.0194	1.24	6.8
0.0386	0.0194	8.8	6.0
0.0772	0.0194	28.0	6.7

Mean value 6.8

[a] $k_{2.5}$ (l.$^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$) for production of silver bromide in the reaction between 2-octyl bromide and silver nitrite in acetonitrile at 44.6°.

Table VII. Effect of Added Tetraethylammonium Nitrite on the Initial Velocity of Silver Bromide Production[a]

[Et$_4$NNO$_2$], M	$10^8 V_i$	[Et$_4$NNO$_2$], M	$10^8 V_i$
0.0000	3.3	0.0208	18.5
0.0042	3.9	0.0261	39.4
0.0078	5.0	0.0306	59.9
0.0104	6.2	0.0383	84.6
0.0131	7.8	0.0436	128
0.0174	11.4	0.0582	186
0.0192	15.1	0.0739	259

[a] V_i (mole l.$^{-1}$ sec.$^{-1}$) in the reaction between (0.0193 M) 2-octyl bromide and (0.0193 M) silver nitrite in acetonitrile at 44.6°.

Figure 9. Effect of added Et$_4$NNO$_2$ on the initial rate of reaction, V (mole l.$^{-1}$ sec.$^{-1}$), between 2-octyl bromide (0.0193 M) and AgNO$_2$ (0.0193 M) in CH$_3$CN at 44.6°.

dramatic increase in the reaction velocity as indicated in Figure 9. We have analyzed these results as follows. Initially most of the added nitrite ions will complex with free AgNO$_2$ to form the Ag(NO$_2$)$_2^-$ anion. This would take place until all the silver ions will be complexed; when further nitrite ions are added they would be essentially free to attack the 2-octyl bromide. The slope of the limiting linear increase as further tetraethylammonium nitrite is added will be determined by the second-order coefficient for this reaction, k_2 (see section 3). The value obtained for the limiting slope dV/d[Et$_4$NNO$_2$] is 4.60 × 10^{-5} sec.$^{-1}$, leading to k_2 = 4.60 × 10^{-5}/0.0193 = 2.38 × 10^{-3} l. mole^{-1} sec.$^{-1}$. This value is in good agreement with the value previously obtained at 44.6° for the second-order coefficient in the reaction between 2-octyl bromide and tetraethylammonium nitrite, 2.13 × 10^{-3} l. mole^{-1} sec.$^{-1}$.

The relatively small rise in initial velocity with added tetraethylammonium nitrite for concentrations of tetraethylammonium nitrite below that of silver nitrite cannot be treated quantitatively. Indeed, it is not known to what extent it results from a speeding up of the silver-assisted mechanism by added nitrite ions and to what extent it is due to an S_N2 process involving a few uncomplexed nitrite ions.

Discussion

The reaction of 2-octyl bromide with Et$_4$NNO$_2$ in solvent acetonitrile was found to have second-order kinetics, first order in each reactant, and is presumably an S_N2 process. The ratio of the second-order rate
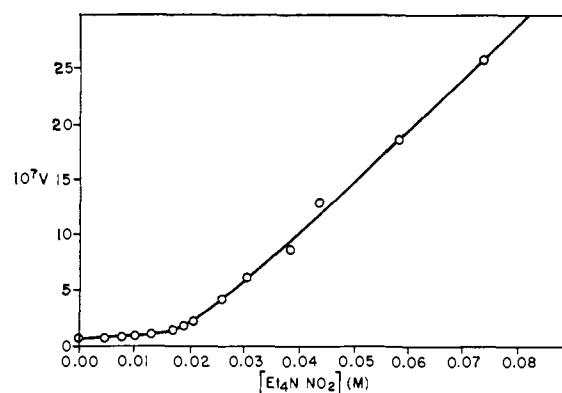
coefficients at 44.6° for attack by nitrate ions and by nitrite ions is 1:490. The reaction of 2-octyl bromide with tetraethylammonium nitrate has a frequency factor of 10$^{9.3}$ and with tetraethylammonium nitrite a frequency factor of 10$^{9.1}$; these values are not markedly different and the large rate difference arises almost entirely from the respective activation energies of 21.4 kcal./mole for attack by tetraethylammonium nitrate as opposed to 17.2 kcal./mole for attack by tetraethylammonium nitrite.
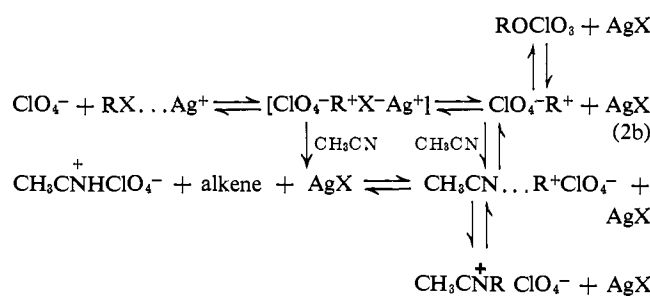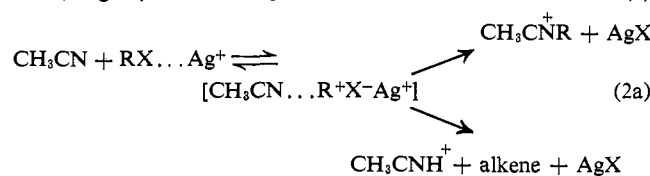
Despite the fact that the attack of the rather weakly nucleophilic nitrate ions on 2-octyl bromide in solvent acetonitrile is an S_N2 process, it would be surprising if a similar bimolecular attack could occur with perchlorate ions acting as a nucleophilic reagent. At 100.1° a solution of 2-octyl bromide in acetonitrile was found to produce bromide ions in the absence of any additives. The addition of tetraethylammonium perchlorate at this temperature accelerated this reaction, but the acceleration did not show any simple or even constant order in tetraethylammonium perchlorate and the effect of added perchlorate could be best described as a salt effect on the "solvolysis" of 2-octyl bromide. The reaction consists of about 85% elimination irrespective of whether added perchlorate is present and about 15% substitution probably derived from bromide ion displacement by the solvent. The reaction of 2-octyl bromide with acetonitrile could be unimolecular proceeding via a carbonium ion intermediate which then partitions between substitution and elimination. Alternatively, it could involve a bimolecular process involving attack by the solvent via S_N2 and E2 mechanisms. Both the unimolecular and the bimolecular mechanisms are consistent with the observed first-order kinetics. Also, since in both mechanisms the transition states are respectively more polar than the initial states, both account equally well for the marked acceleration produced by added tetraethylammonium perchlorate.

The reaction of 2-octyl bromide with AgClO$_4$ proceeds at a slower rate than its reaction with a corresponding concentration of AgNO$_3$. Conductance measurements show that AgClO$_4$ is at any given concentration more dissociated than AgNO$_3$, and if the rate-determining step of the reaction merely involved a free Ag$^+$ and a 2-octyl bromide molecule, then the reaction with AgClO$_4$ would be expected to be faster than

that with AgNO₃. It is quite clear from this result alone that the anion must be capable of intervening in the rate-determining step. The order in 2-octyl bromide is unity but the order in AgClO₄ is somewhat complex; as the concentration of AgClO₄ becomes very low (>0.002 M), the order in AgClO₄ tends toward unity, but as the concentration of AgClO₄ increases, so does its order, until with 0.3 M AgClO₄ the order is just over 2. This behavior is completely at variance with that observed when AgNO₃ is attacking 2-octyl bromide. In the limiting case, *i.e.*, when an order of unity is observed in both 2-octyl bromide and in stoichiometric AgClO₄, there appears to be no intervention by ClO₄⁻ in the rate-determining step. This observation is consistent with a mechanism involving electrophilic assistance by both free and paired Ag⁺ with either no nucleophilic assistance at all or with the nucleophilic assistance of CH₃CN in the rate-determining step.

As the concentration of AgClO₄ increases, the order also increases, a behavior which can be analyzed by a superposition of two reaction paths, one being assisted by CH₃CN, the other being assisted by ClO₄⁻. In order to account for the order in AgClO₄ rising to 2, or even above 2, it is necessary to assume that the negative ionic strength effect associated with the transition state involving ClO₄⁻ intervention in the rate-determining step (2b) is more than compensated for by the positive salt effect caused by dissociated AgClO₄ in the solvent assisted ionization process (2a) (Scheme

Scheme I

$$RX + Ag^+ \rightleftharpoons RX\ldots Ag^+ \tag{1}$$

$$CH_3CN + RX\ldots Ag^+ \rightleftharpoons$$
$$[CH_3CN\ldots R^+X^-Ag^+] \tag{2a}$$

$$\nearrow CH_3\overset{+}{C}NR + AgX$$
$$\searrow CH_3CN\overset{+}{H} + alkene + AgX$$

$$ROClO_3 + AgX$$
$$\big\Updownarrow$$
$$ClO_4^- + RX\ldots Ag^+ \rightleftharpoons [ClO_4^-R^+X^-Ag^+] \rightleftharpoons ClO_4^-R^+ + AgX \tag{2b}$$
$$\big\downarrow CH_3CN \quad CH_3CN \big\Updownarrow$$
$$CH_3\overset{+}{C}NHClO_4^- + alkene + AgX \rightleftharpoons CH_3CN\ldots R^+ClO_4^- + $$
$$\big\Updownarrow \quad AgX$$
$$CH_3\overset{+}{C}NR \; ClO_4^- + AgX$$

I). The symbol Ag⁺ is used to represent both free and paired silver ions irrespective of their state of solvation in acetonitrile; a more accurate description of step 1 would probably be RX + Ag(NCCH₃)⁺₂ ⇌ CH₃CN + [RXAgNCCH₃]⁺.
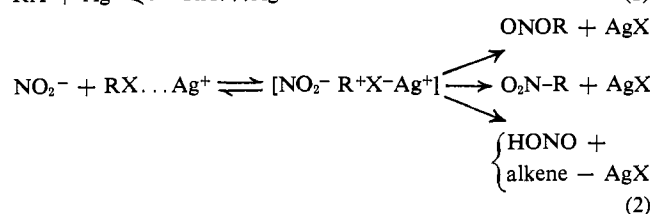
Although covalent 2-octyl perchlorate may well be formed in small amounts, it is unlikely that it will be built up in any appreciable concentration because of the relative slowness of the rate-determining step leading to its production from 2-octyl bromide. Covalent perchlorates can be considered as a source of carbonium ions (or of carbonium perchlorate ion pairs) which in turn react with CH₃CN to yield CH₃C≡N⁺RClO₄⁻. These ionic perchlorates hydrolyze with extreme ease to the corresponding amides (CH₃-CONHR), and we were able to isolate *sec*-octyl acetamide. Alternatively, these carbonium ions can

transfer a proton to CH₃CN and yield olefins. Silver perchlorate leads to a higher degree of olefin production than silver nitrate, and it was also found that the olefinic proportion of the products fell as the reaction proceeded. Accompanying olefin formation is the production of perchloric acid; the hydrogen ions present in a solution of this strong acid combine with olefin molecules to yield carbonium ions which in part (reversibly) merely transfer a proton to CH₃CN to regenerate olefin, but which in part react *irreversibly* with CH₃CN with loss of olefin from solution. A consideration of the olefin proportion produced in the initial stages of the reaction shows a slight tendency for elimination to be favored as the concentration of AgClO₄ increases. For a given concentration of silver perchlorate, the value for the olefin proportion rises as the temperature rises.

Although added Et₄NClO₄ decreases the rate of reaction of 2-octyl bromide with AgNO₃, it is to be expected on the scheme put forward that it will increase the rate of reaction with AgClO₄, and this is in fact found. The increase in rate was shown not to be simply related either to the total stoichiometric concentration of ClO₄⁻ or to the concentration of free ClO₄⁻. This is not surprising since in the Ag⁺-catalyzed reaction the component of reaction in which CH₃CN intervenes (Scheme I, step 2a) and the one in which ClO₄⁻ intervenes (Scheme I, step 2b) occur side by side but are subject to opposing ionic strength effects. The olefin proportion of the products shows only a small increase on adding Et₄NClO₄, and this increase is of the same order of magnitude as that observed on increasing [AgClO₄] alone.

The reaction of 2-octyl bromide with AgNO₂ is of 2.5 order, similar to that of AgNO₃ but slower; the ratio $V_{AgNO_2}:V_{AgNO_3} = 1:3.8$ at 44.6°. Also the rate of attack is slower than that by an equivalent concentration of Et₄NNO₂; $V(0.02\ M\ AgNO_2):V(0.02\ M\ Et_4NNO_2) = 1:24$ at 44.6°. These comparisons strongly indicate that only a few nitrite ions are free.[1] A kinetic pattern postulating AgNO₂ and Ag⁺ acting as electrophiles with free NO₂⁻ acting as a nucleophile may account for the 1.5 order in AgNO₂ (Scheme II).

Scheme II

$$RX + Ag^+ \rightleftharpoons RX\ldots Ag^+ \tag{1}$$

$$NO_2^- + RX\ldots Ag^+ \rightleftharpoons [NO_2^- R^+X^-Ag^+]$$
$$\nearrow ONOR + AgX$$
$$\longrightarrow O_2N-R + AgX$$
$$\searrow \begin{cases} HONO + \\ alkene - AgX \end{cases} \tag{2}$$

The effect of adding Et₄NNO₂ shows that the suggested pattern for the dissociation of AgNO₂ is fundamentally correct; at first the rate remains low due to the formation of Et₄N⁺Ag(NO₂)₂⁻, but when essentially all the silver is present as the dinitrito complex, then the rate increases dramatically due to the fact that the nitrite ions now added remain *free* and react with 2-octyl bromide by a simple SN2 process.

Experimental Section

Materials. The materials employed in this work have been purified and dried as described in the Experimental Section of part III in this series.[1]

Table VIII. Integrated Second-Order Rate Coefficients[a]

(i) [AgClO$_4$] = 0.00206 M									
Time, min.	0	820	1360	2280	2810	3700	4280	5160	5930
Reaction, %[b]	1.0	7.0	11.2	16.9	20.2	24.8	28.5	33.1	35.7
$10^5 k_2$	...	3.36	3.51	3.41	3.41	3.30	3.38	3.38	3.35
(ii) [AgClO$_4$] = 0.0447 M									
Time, min.	0	878	1130	1420	2340	2560	3380		
Reaction, %[c]	0.3	11.4	15.1	17.3	26.2	28.6	37.0		
$10^5 k_2$	...	5.20	5.67	5.30	5.40	5.55	5.33		
(iii) [AgClO$_4$] = 0.179 M									
Time, min.	0	104	190	370	518	1400	2020		
Reaction, %[c]	3.8	19.2	28.9	47.3	57.6	87.8	95.1		
$10^5 k_2$	...	15.0	14.4	14.9	14.7	13.6	11.4		

[a] k_2 (1. mole^{-1} sec.$^{-1}$) of AgBr production in the reaction of 2-octyl bromide (0.0378 M) with AgClO$_4$ in CH$_3$CN at 60.0°. [b] The per cent reaction is expressed in terms of the silver perchlorate. [c] The per cent reaction is expressed in terms of the 2-octyl bromide.

Kinetic Techniques. All the runs reported in this paper have been carried out using the sealed bulb technique reported in part III of this series.[1]

Measurement of the Over-all Rate of Reaction. All runs in which the over-all rate of reaction of the alkyl halide, $-d[RBr]/dt$, has been followed, have been analyzed by potentiometric titration in order to determine directly either $d[Br^-]/dt$ or $-d[Ag^+]/dt$. Since the reaction of 2-octyl bromide with silver perchlorate was found in the limit to exhibit second-order kinetics, first order in each reactant, the analysis was in this case carried out in terms of integrated second-order rate coefficients (see Table VIII) and in runs in which a downward trend in the second-order rate coefficient could be discerned, an extrapolation to zero reaction was carried out.

Extent of Olefin Formation. Although the extent of acid formation in aprotic solvents is frequently identical with the extent of olefin formation, there are cases, *e.g.*, the reaction of 2-octyl bromide with AgClO$_4$ in CH$_3$CN, where the two quantities differ. In these cases the proportion of olefin produced has to be determined directly. This was conveniently carried out by determining the amount of bromine which adds to the olefin.[17] The contents of the sealed tube was washed out with distilled water into 20 ml. of Analar glacial acetic acid. A standard solution of bromine in Analar glacial acetic acid was then added in excess of the amount required and then, after a few seconds, an excess of solid Analar potassium iodide was added followed by distilled water to make the bulk up to 100 ml. The iodine liberated from the potassium iodide by the excess bromine was titrated against standard sodium thiosulfate solution, using starch as an indicator. In this titration medium starch was found to be a more satisfactory indicator than sodium starch glycollate. The amount of bromine disappearing prior to the addition of the potassium iodide gives a direct measure of the extent of olefin production. In the absence of silver salts the titration was straightforward, but when silver salts were present in solution, addition of potassium iodide precipitated the silver ions as silver iodide and gave the titration mixture a pale yellow cloudiness. In these cases the end point was identified with the change from blue to a pale yellow cloudiness, and not to the normal colorless solution which is obtained when silver salts are absent.

(17) V.p.c. analysis[18] after *ca.* 23 % reaction has confirmed the presence of octenes (2-octene:1-octene ≈ 9:4) in amounts essentially identical with those estimated by the bromination procedure, thus excluding CH$_2$=C=NR as a reaction product in the initial stages of the reaction.

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