Electrophilic Catalysis in Nucleophilic Substitution and Elimination. VI. The Reaction of Silver Perchlorate and of Silver Perchlorate–Tetra-n-butylammonium Perchlorate Mixtures with 2-Octyl Bromide in Benzene[1,2]

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The reaction between silver perchlorate and 2-octyl bromide in benzene is first order in alkyl halide but of variable order in $AgClO_4$. At low concentrations of salt, a limiting order of 1.5 in $AgClO_4$ is obtained. In this region extremely small quantities of $n\text{-}Bu_4NClO_4$ have a profound accelerative effect, but a limiting velocity is soon attained. As the concentration of $AgClO_4$ is increased the maximum rate enhancement by added $n\text{-}Bu_4NClO_4$ is reduced. The reaction products are a mixture of olefins and 2-octyl perchlorate ester. Silver perchlorate converts (+)-2-octyl bromide into (−)-2-octyl perchlorate with 60% retention of optical purity in the inversion, irrespective of the silver perchlorate concentration or whether $n\text{-}Bu_4NClO_4$ is added. The rates are analyzed in terms of concurrent reactions whose activated complexes have the limiting stoichiometric composition RX, $2(Ag^+ClO_4^-)$ and RX, $(Ag^+ClO_4^-)$-$(n\text{-}Bu_4N^+ClO_4^-)$. It is suggested that these concurrent reactions lead to the same quadruple ion intermediate $(ClO_4^-R^+Br^-Ag^+)$; and that the steric result is compatible with semirigidly oriented quadruple ions.

Introduction

In nonsolvolytic media the stoichiometric composition of the activated complex is more clearly defined, the possible topological structures of the transition state are more easily scrutinized, and very short-lived intermediates are not captured *irreversibly* by a solvent molecule in the solvation cage.[4] Therefore considerable interest is to be attached to silver ion assisted substitutions of alkyl halides under conditions in which solvolysis is excluded by the use of aprotic media. Originally we have carried out such studies in acetonitrile[1,5–7] using $AgNO_3$, $AgNO_2$, and $AgClO_4$, but found that with the latter, nucleophilic solvent intervention effectively competes with ClO_4^- participation. We were therefore interested in studying the nature of the electrophilic catalysis by $AgClO_4$ in a hydrocarbon solvent in which the

covalent perchlorate esters once formed would be sufficiently stable. Redies and Iredale[8] have investigated the reaction of methyl iodide with silver perchlorate in benzene and claimed an over-all order of 2.5 made up as follows: $V = k_{2.5}[CH_3I]^{1.0}[AgClO_4]^{1.5}$. In view of the fairly complex electrochemical behavior of $AgClO_4$ in benzene[9] this is a somewhat surprising result because investigations of ionic reactions in benzene indicate that formal kinetic order varies with electrolyte concentration.[10] Burton and Praill[11] have shown that the production of methyl perchlorate is accompanied by very small amounts of toluene, *i.e.*, that the nucleophilic solvent intervention is sufficiently small to allow most of the carbonium perchlorate ion pairs to collapse to perchlorate ester.

Although no mechanistic studies have so far been reported on perchlorate esters, it is important to note the special salt effects observed by Winstein, *et al.*,[12] for the addition of $LiClO_4$ on the acetolysis of certain tosylates. They postulate an exchange reaction between two ion pairs: $R^+_{\|}OTs^- + Li^+ClO_4^- = R^+_{\|}ClO_4^- + Li^+OTs$, leading to carbonium perchlorate ion pairs which undergo acetolysis in preference to collapse. It is also instructive to examine the catalysis by *dissociated perchlorate ions* of the methanolysis of trityl chloride in benzene.[13]

If the generally assumed low aptitude of carbonium-perchlorate ion pairs for collapse is right, it must be conceded that in *dry benzene* collapse of carbonium perchlorate ion pairs to perchlorate esters occurs because of the low dielectric constant, the low solvating capacity, and the low nucleophilicity of the solvent. Use of 2-octyl bromide permits optical studies and we have sought evidence on the mechanism of the reaction of 2-octyl bromide with $AgClO_4$ in benzene by studying it in two successive stages: (a) by defining the stoichiometric composition (*i.e.*, the empirical formula) of the activated complex and (b) by determining the topology and the geometry of the transition state.

(1) Part V: Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4778 (1965).

(2) Taken in part from the research report submitted by Dennis N. Kevill during the tenure of a Temporary Assistant Lectureship at University College.

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(5) Part III: Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4760 (1965).

(6) 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).

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Results

1. *The Over-All Rate of Reaction.* 2-Octyl bromide reacts with silver perchlorate in benzene at conveniently measurable speeds at 25.0°. The reaction is easily quenched by the introduction of samples into an excess of dry acetonitrile. Samples treated in this way could be kept for several hours at room temperature without detectable change in the concentration of the silver ion remaining in solution. Also any 2-octyl perchlorate formed, which could interfere with the subsequent potentiometric titration against standard potassium chloride: $RClO_4 + Cl^- \rightarrow RCl + ClO_4^-$, is rapidly solvolyzed by acetonitrile prior to titration. Throughout each individual run a marked autocatalysis is observed and this necessitated an analysis in terms of initial rates. Runs were carried out by direct sampling from the bulk reaction mixture. In the initial stages of reaction the precipitated silver bromide remained dispersed throughout the entire solution; only much later did it coagulate and form a precipitate at the bottom of the flask. The reaction is first order in 2-octyl bromide. This was shown for a constant concentration of silver perchlorate (0.0145 M) and varying 2-octyl bromide concentration within the range 0.01–0.08 M (Table I). On the other hand, the order in silver perchlorate is not constant; it increases as its concentration increases, but for low concentrations the order approaches a limiting value of 1.5 in $AgClO_4$: initial velocity $(V_i) = k_{2.5}[\text{2-OctBr}] \cdot [AgClO_4]^{1.5}$.

Table I. Initial First-Order Rate Coefficients, k_1, (sec.$^{-1}$) and Initial 2.5-Order Rate Coefficients, $k_{2.5}$ ($l.^{1.5}$ mole$^{-1.5}$ sec.$^{-1}$), for Silver Bromide Production in the Reaction of 2-Octyl Bromide with Silver

[2-OctBr], M	[AgClO$_4$], M	$10^6 k_1{}^a$	$10^2 k_{2.5}{}^a$
0.0100	0.00104	0.89	2.6
0.0100	0.00122	0.92	2.2
0.0100	0.00122	0.96	2.3
0.0200	0.00182	1.8	2.3
0.0100	0.00224	2.5	2.4
0.0200	0.00224	3.0	2.8
0.0200	0.00224	3.0	2.8
0.0200	0.00363	6.0	2.7
0.0200	0.00482	8.9	2.7
0.0400	0.00725	16.0	2.6
0.0200	0.00964	26	2.7
0.0400	0.0122	46	3.4
0.0100	0.0145	58	3.3
0.0200	0.0145	68	3.9
0.0400	0.0145	61	3.5
0.0800	0.0145	64	3.7
0.0400	0.0241	152	4.1
0.0400	0.0358	263	3.9
0.0400	0.0488	483	4.5
0.0800	0.0671	1000	5.8
0.0400	0.0975	1780	5.8

^{a} $-d[RBr]/dt = -dAg^+/dt = d[AgBr]/dt = k_1[RBr] = k_{2.5} [RBr]^{1.0}[AgClO_4]^{1.5}$

A logarithmic plot of the first-order rate coefficients with respect to 2-octyl bromide against the concentration of silver perchlorate is given in Figure 1. The slope at any point gives the order in silver perchlorate for the concentration involved. Added tetra-*n*-butylammonium perchlorate accelerates the reaction of silver perchlorate with 2-octyl bromide in benzene at 25.0°.
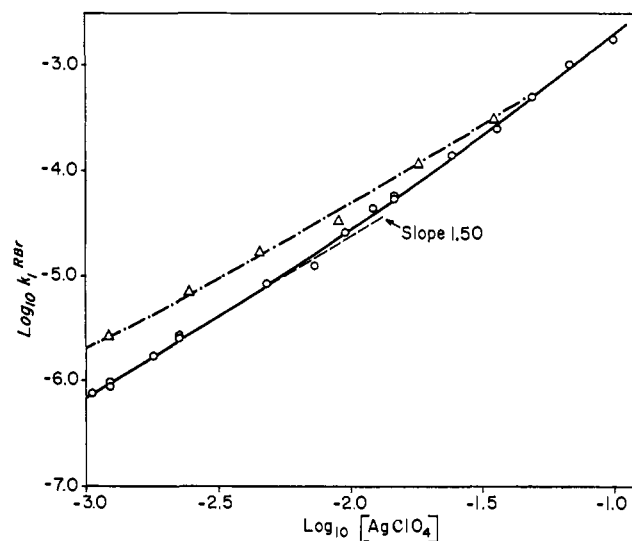

Figure 1. Reaction of 2-octyl bromide with silver perchlorate in benzene at 25.0°; plot of the logarithm of the initial specific rate of disappearance of 2-octyl bromide *vs.* the logarithm of the silver perchlorate concentration: O, without any other salt except AgClO$_4$; △, with added *n*-Bu$_4$NClO$_4$.

Extremely small quantities of tetra-n-butylammonium perchlorate were found to have a profound accelerative effect. However, for a constant concentration of 2-octyl bromide and of silver perchlorate a maximum velocity was soon attained and addition of further quantities of tetra-*n*-butylammonium perchlorate produced no further rate increase. For a concentration of silver perchlorate of 0.00122 M, and of 2-octyl bromide of 0.010 M, the initial reaction velocity is increased by a maximum factor of about 2.6 by the addition of tetra-*n*-butylammonium perchlorate (Table II).

Although in the region of "maximum perchlorate ion catalysis" the initial reaction velocities are virtually identical, the extent of reaction after a given time can be seen to become less autocatalyzed as the concentration of tetra-*n*-butylammonium perchlorate increases (Table III). The autocatalysis is probably due to the perchloric acid produced in this reaction. (It acts as an electrophilic catalyst: $RBr + HClO_4 \rightarrow R^+ClO_4^- + HBr$, which is constantly regenerated: $HBr + AgClO_4 \rightarrow AgBr + HClO_4$. The addition of *n*-Bu$_4N^+$ ClO$_4^-$ might remove $HClO_4$ from benzene and produce ion pairs which contain the nonelectrophilic anion-$H(ClO_4)_2^-$. This is only a hypothesis, but it has a parallel in the reduction of the HCl catalysis by added tetra-*n*-butylammonium chloride in benzene.[13])

Two complimentary series of runs were carried out. In one the concentration of silver perchlorate was varied; in the other a sufficiently high concentration of tetra-*n*-butylammonium perchlorate was added to the silver perchlorate present to obtain the limiting velocity increase. The first-order rate coefficients (with respect to 2-octyl bromide) of the two complimentary series of runs are compared in Table IV. It will be noticed that the rate enhancement produced by added tetra-*n*-butylammonium perchlorate is much more pronounced at low [AgClO$_4$]; it becomes negligibly small when [AgClO$_4$] > 0.05 M.

The logarithmic plot of $k_1{}^{max}$ against [AgClO$_4$] (in the presence of fairly small concentrations of tetra-

Table II. Effects of Added n-Bu$_4$NClO$_4$ upon the Initial First-Order Rate Coefficient, k_1 (sec.$^{-1}$), for Silver Bromide Formation with Respect to 2-Octyl Bromide[a]

$10^6[n$-Bu$_4$NClO$_4]$	0.00	0.00	3.1	31.3	125	625
$10^6 k_1$	0.9	1.0	2.0	2.7	2.6	2.5
$10^6[n$-Bu$_4$NClO$_4]$	625	2500	5000	5000	7500	
$10^6 k_1$	2.6	2.3	2.5	2.4	2.6	

[a] [2-OctBr] = 0.010 M; [AgClO$_4$] = 0.00122 M; solvent, benzene; temperature, 25.0°.

Table III. The Reaction of 0.0100 M 2-Octyl Bromide with 0.00122 M Silver Perchlorate in the Presence of Tetra-n-butylammonium Perchlorate in Benzene at 25.0°

(A) [n-Bu$_4$NClO$_4$], absent

Time, min.	0	20	40	60	80	100	120	140
Reaction, %[a]	0.0	1.1	2.5	3.9	6.4	10.8	15.6	18.1
$10^5 k_1'$		0.9	1.0	1.0	1.3	1.8	2.2	2.2

Initial k_1' 0.8 × 10^{-5} sec.$^{-1}$; initial velocity 1.0 × 10^{-8} mole l.$^{-1}$ sec.$^{-1}$

(B) [n-Bu$_4$NClO$_4$], 0.0000313 M

Time, min.	0	15	30	45	60	75	90	105
Reaction, %[a]	0.0	2.3	4.9	8.1	12.5	16.6	23.4	29.9
$10^5 k_1'$		2.6	2.8	3.1	3.7	4.0	4.9	5.8

Initial k_1' 2.2 × 10^{-5} sec.$^{-1}$; initial velocity 2.7 × 10^{-8} mole l.$^{-1}$ sec.$^{-1}$

(C) [n-Bu$_4$NClO$_4$], 0.00500 M

Time, min.	0	15	30	45	60	75	90	105
Reaction, %[a]	0.0	1.9	3.9	5.3	8.3	10.6	12.1	13.9
$10^5 k_1'$		2.1	2.2	2.0	2.4	2.5	2.4	2.4

Initial k_1' 2.0 × 10^{-5} sec.$^{-1}$; initial velocity 2.5 × 10^{-8} mole l.$^{-1}$ sec.$^{-1}$

[a] Expressed in terms of silver perchlorate: k_1' (sec.$^{-1}$) is the integrated first-order rate coefficient with respect to silver perchlorate.

Table IV. Comparison of the Initial First-Order Rate Coefficients for Reaction of Silver Perchlorate with 2-Octyl Bromide in Benzene at 25.0°, k_1 (sec.$^{-1}$), with Those Obtained in the Presence of Sufficient Tetra-n-butylammonium Perchlorate to Observe Maximum Velocity Increase, k_1^{max} (sec.$^{-1}$)

[2-OctBr], M	[AgClO$_4$], M	[n-Bu$_4$N-ClO$_4$], M	$10^6 k_1$[a]	$10^6 k_1^{max}$[b]	$\dfrac{k_1^{max}}{k_1}$
0.0100	0.00122	0.000625	0.9	2.5	2.6
0.0100	0.00244	0.000625	3.0	7.0	2.3
0.0100	0.00450	0.000625	7.6	16	2.1
0.0100	0.00900	0.000625	25	34	1.4
0.0200	0.00180	0.00500	83	124	1.5
0.0200	0.0350	0.00500	260	307	1.2

[a] In the absence of n-Bu$_4$NClO$_4$. [b] In the presence of the recorded amount of n-Bu$_4$NClO$_4$.

n-butylammonium perchlorate necessary to obtain k_1^{max}) (broken line, Figure 1) shows that although for low silver perchlorate concentrations the limiting order in silver perchlorate falls below 1.5, it only falls to a value of about 1.4 at the lowest concentration considered (0.00122 M).

2. The Partial Rates of Elimination and of Substitution. In the reaction of 2-octyl bromide with AgClO$_4$ in benzene the expected products in addition to silver bromide are: (a) 2-octyl perchlorate, (b) a mixture of 1-octene and 2-octene accompanied by perchloric acid, and (c) 2-phenyloctane accompanied by perchloric acid.

a. Partial Rate of 2-Octyl Perchlorate Formation. Acid production does not accompany the formation of 2-octyl perchlorate. However, the latter is very vulnerable to nucleophilic attack and must be destroyed without acid production; any elimination at this stage would invalidate the required measurement. Consequently, prior to the titration of acid, the 2-octyl per-

chlorate was destroyed by reaction with a solution of lithium chloride in dry neutral acetone.

We have also established that changing the method of destruction of the 2-octyl perchlorate had no effect upon the subsequent acid determination. Thus two other neutral salts were used and the solvent conditions were also varied. (i) Treatment of each aliquot with tetraethylammonium bromide dissolved in neutral acetone–acetonitrile mixture (6:1) leads to identical titrimetric values with those obtained in the treatment of aliquots with lithium chloride in acetone. (ii) The treatment of each aliquot with tetraethylammonium nitrate dissolved in acetonitrile and the subsequent (after 2 hr.) addition of a solution of lithium chloride in neutral acetone (to precipitate silver ions remaining in solution) again leads to titrimetric values identical with those obtained by treating the aliquots with lithium chloride in acetone. It seems that under all three conditions for the destruction of the 2-octyl perchlorate a clean substitution (probably S$_N$2) between the anion of the neutral salt and the 2-octyl perchlorate is operative. It would be surprising if elimination accompanied the destruction of 2-octyl perchlorate by Cl$^-$, Br$^-$, or NO$_3^-$ since the ratios of elimination to substitution for all three nucleophiles under different solvent conditions are identical. We consequently assume that the 2-octyl perchlorate is destroyed without accompanying acid formation.

In the reaction of 2-octyl bromide with silver perchlorate in solvent benzene at 25.0° (see Table V) it was found that the percentage of reaction which had taken place with acid formation was a constant[14]

(14) After coagulation of the silver bromide the titers became subject to random error and this was found to be due to the absorption of the perchloric acid by the silver bromide precipitate and the titers were dependent upon the varying amounts of precipitate included in the sample. Values for the proportion of reaction with acid formation were therefore obtained during the initial stages of reaction, while the AgBr was in a dispersed (colloidal) form.

independent of the extent of reaction. It was further found that this constant value for the percentage of reaction with acid formation was identical from run to run, independent of the initial reactant concentrations.

Table V. The Proportion of 2-Octyl Perchlorate Formed in the Reaction of 2-Octyl Bromide with Silver Perchlorate in Benzene at 25.0°[a]

[2-OctBr], M	[AgClO$_4$], M	[n-Bu$_4$N-ClO$_4$], M	A_{max}, %[b]	P, %[c]
0.0100	0.00104	...	10	60
0.0100	0.00122	...	15	60
0.0100	0.00122	0.00031	10	63
0.0100	0.00122	0.0031	15	64
0.0100	0.00122	0.0125	15	64
0.0100	0.00122	0.0625	40	58
0.0100	0.00122	0.2500	10	60
0.0100	0.00122	0.5000	15	61
0.0100	0.00122	0.7500	15	58
0.0200	0.00182	...	35	64
0.0200	0.00224	...	25	64
0.0200	0.00482	...	25	64[d]
0.0200	0.00964	...	10	61[e]
0.0400	0.0122	...	10	58
0.0400	0.0241	...	20	58
0.0400	0.0488	...	20	60
0.0800	0.0671	...	40	61
0.0400	0.0975	...	30	57

[a] The mean value for 2-octyl perchlorate formation is 61%. [b] A_{max} is the extent of total possible AgBr production for which 2-octyl perchlorate formation was followed titrimetrically. [c] P = ([2-OctOClO$_3$] × 100)/[total reaction] = ([2-Oct OClO$_3$] × 100)/[AgBr]. [d] Identical value obtained when NEt$_4$Br used to decompose 2-octyl perchlorate. [e] Identical value when NEt$_4$NO$_3$ used to decompose 2-octyl perchlorate.

b. Partial Rate of Olefin Formation. After treating aliquots with lithium chloride in acetic acid, the olefin was determined by direct bromination. The treatment with lithium chloride had a double purpose: it destroyed by substitution (no elimination) any 2-octyl perchlorate and it also precipitated excess silver ion. Under these conditions the reaction of 2-octyl bromide with silver perchlorate in solvent benzene at 25.0° proceeds with *ca.* 38% olefin formation throughout each run (Table VI), a constant independent of the extent of reaction and essentially independent of the initial reagent concentration.

Table VI. The Olefin Proportion of the Products (E) for Various Initial Reactant Concentrations in the Reaction of 2-Octyl Bromide with Silver Perchlorate in Benzene at 25.0°

[2-OctBr], M	[AgClO$_4$], M	A_{max}, %[a]	E, %[b]
0.0400	0.00725	100	35
0.0400	0.0145	70	39
0.0400	0.0358	35	41
0.0800	0.0671	50	37

[a] A_{max} is the extent of total possible silver bromide production for which olefin formation was also followed. [b] The mean value for olefin formation is 38%.

c. 2-Phenyloctane Formation. The reaction leading to the formation of 2-octyl perchlorate is *ca.* 61% of the total and the reaction leading to olefin formation is *ca.* 38% of the total. Any 2-phenyloctane which may be formed cannot account for more than a very small proportion of the products. This is consistent with earlier findings[15] which indicate that only extremely small quantities of alkylated benzene are produced when secondary alkyl halides react with silver perchlorate in benzene.

3. 2-Octyl Perchlorate in Acetonitrile–Benzene Mixtures. A solution of 2-octyl perchlorate in benzene was prepared by allowing a solution of 0.107 M 2-octyl bromide and 0.0790 M silver perchlorate to react at 25.0°. Olefin and perchloric acid are also formed but a considerable proportion of the acid is lost, by absorption upon the precipitate, when the silver bromide is filtered off. The filtrate was shown by potentiometric titration to contain no remaining silver ion. Solutions in acetonitrile–benzene mixtures were made up by a series of suitable dilutions of the filtrate at 25.0°. The rate of decomposition of the 2-octyl perchlorate was determined by removing aliquots at various intervals and introducing them into a neutral solution of lithium chloride in acetone and titrating against sodium methoxide in methanol using lacmoid as indicator. 2-Octyl perchlorate remaining at sampling time is destroyed without acid formation being quantitatively converted into 2-octyl chloride and LiClO$_4$. Decomposition of 2-octyl perchlorate prior to sampling will be reflected as an increase in the initial acid concentration since both olefin formation and N-alkylation of the acetonitrile will be accompanied by acid formation when the mixture is titrated against MeO$^-$–MeOH.

Our studies show that solutions of 2-octyl perchlorate in benzene were stable over at least 4 days, the acid concentration remaining unaltered over this period. The half-lifetime of 2-octyl perchlorate diminishes rapidly as the proportion of acetonitrile relative to benzene is increased. Thus the half-lifetime at 25° varies from 180 min. in 10% CH$_3$CN–90% C$_6$H$_6$ (by volume) to 3.6 min. in 50% CH$_3$CN–50% C$_6$H$_6$ (by volume) to 0.9 min. in 90% CH$_3$CN–10% C$_6$H$_6$ (by volume).

Account being taken of the rapid rate of decomposition of 2-octyl perchlorate in 90% CH$_3$CN–10% C$_6$H$_6$, it can be seen that in pure acetonitrile the rate of decomposition of 2-octyl perchlorate will be many times faster than its rate of formation from silver perchlorate and 2-octyl bromide in this solvent. (The latter reactions are relatively much slower even at temperatures higher than 25.0°.) Our present measurements confirm the correctness of regarding any 2-octyl perchlorate formed in acetonitrile as an unstable intermediate.[7]

4. Stereochemistry of Reaction. The reaction of 2-octyl bromide with silver perchlorate in benzene has been found to proceed with 61% 2-octyl perchlorate formation and 38% olefin formation. The olefins will be optically inactive but it is possible that the 2-octyl perchlorate may possess optical activity. A benzene solution 0.135 M in both 2-octyl bromide and silver perchlorate was left for 1 hr. at 25.0°, after which time the reaction had essentially gone to completion; it was then filtered, but the filtrate quickly became turbid. Despite several attempts, it was not possible to

(15) H. Burton, D. A. Munday, and P. F. G. Praill, *J. Chem. Soc.*, 3933 (1956).

Table VII. Concurrent Polarimetric and Titrimetric Studies of the Interconversion
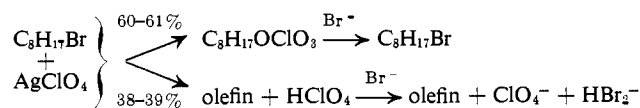
(+)-2 OctBr $\xrightarrow{\text{AgClO}_4}$ (−)-2-OctOClO$_3$ $\xrightarrow{\text{Br}^-}$ (+)-2-OctBr

A[a]

Time, min.	0	2	5	12	30	180
Titer[b]	5.38	2.88	1.53	0.93	0.07	0.00
Rotation[c]	+0.71	+0.54	+0.38	+0.31	+0.28	+0.10
Rotation, 30 sec. later[b]	+0.66	+0.50	+0.37	+0.31	+0.28	+0.10
Loss in rotation[c]	+0.14	+0.30	+0.43	+0.49	+0.52	+0.70
Predicted loss in rotation if reacted 2-OctBr is completely racemized	+0.26	+0.51	+0.65	+0.70	+0.79	+0.80
Rotation of the (+)-2-OctBr formed from (−)-2-OctClO$_4$[d]	+0.12	+0.21	+0.22	+0.21	+0.27	+0.10
Z, %[e,f]		69	56	50	57	21

B[g]

Time, min.	30	60	90	120	180	270	1320
Rotation[h−j]	+0.36	+0.32	+0.28	+0.25	+0.23	+0.23	+0.08

C[k]

Time, min.	0	30	60	120	180	1080
Titer[l]	3.29	1.22	0.00	0.00	0.00	0.00
Rotation[m]	+0.45	+0.28	+0.18	+0.13	+0.09	0.00
Loss in rotation	+0.22	+0.38	+0.49	+0.54	+0.58	+0.67
Predicted loss in rotation if reacted 2-OctBr is completely racemized	+0.33	+0.55	+0.67	+0.67	+0.67	+0.67
Rotation in 2-OctBr formed from 2-OctClO$_4$	+0.11	+0.16	+0.18	+0.13	+0.09	+0.00
Z, %[n,o]	56	49	45	32	22	0

[a] Retention of optical purity (Z) relative to the original (+)-2-octyl bromide, in the (+)-2-octyl bromide formed by the bromide ion attack on the (−)-2-octyl perchlorate produced in the reaction of 0.118 M (+)-2-octyl bromide with 0.118 M silver perchlorate in benzene at 25.0°. [b] Aliquots (2-ml.) for titration against 0.0300 M KCl solution were taken 30 sec. after 5-ml. aliquots for optical rotation, rotations are corrected for this time discrepancy. Titer at *zero reaction* is 7.90 ml. of 0.030 M KCl soln. [c] Rotation at *zero reaction* is 0.80°; polarimeter readings were taken in a 2-dm. polarimeter tube at room temp. [d] (+)-2-OctBr formed by the attack of Br$^-$ on (−)-2-OctOClO$_3$. In C$_6$H$_6$–CH$_3$CN mixture this is a clean displacement process involving no acid formation (*i.e.*, no elimination). [e] Allowing for only 60% 2-OctOClO$_3$ formation. [f] The mean value for retention of optical purity (Z) over the first 30 min. of reaction is 59%. [g] Subsequent racemization of (−)-2-octyl perchlorate formed by the complete reaction of 0.147 M (+)-2-octyl bromide and 0.147 M silver perchlorate in benzene at 25.0°, shown by conversion to (+)-2-octyl bromide. [h] Aliquots 5 ml. into 5 ml. of 0.25 M Et$_4$NBr in acetonitrile. [i] By extrapolation the value for the rotation at zero time is +0.38°. The initial rotation of 0.735 M (+)-2-OctBr in 50% acetonitrile benzene would be +1.00°. [j] Retention of optical purity in the 60% 2-octyl bromide (*i.e.*, allowing for 60% 2-OctOClO$_3$ formation) in the final products is 0.38/1.00 × 100/60, (*i.e.*, 63%). [k] Retention of optical purity (Z) relative to the original (+)-2-octyl bromide, in (+)-2-octyl bromide formed by bromide ion attack upon the (−)-2-octyl perchlorate formed in the reaction of 0.0980 M (+)-2-octyl bromide with 0.0980 M silver perchlorate, in the presence of 0.0067 M tetra-*n*-butylammonium perchlorate in benzene at 25.0°. [l] Aliquots (2 ml.) were taken for titration against 0.030 M KCl solution and 5-ml. aliquots for optical rotation. Titre at *zero reaction* is 6.53 ml. of 0.0300 N KCl solution. [m] Rotation at zero reaction would be +0.67°; measured at room temperature in 2-dm. polarimeter tube. [n] Allowing for only 60% 2-OctOClO$_3$ formation. [o] The initial value for the retention of optical purity (Z) obtained by extrapolation is 57%.

obtain a sufficiently clear solution such that an immediate polarimetric measurement of the optical rotation could be made. After each filtration a small amount of further precipitation occurred. Burton and Munday[16] have postulated soluble complexes between silver chloride and organic perchlorates in acetonitrile and it is possible that complexes of similar structure may be formed in benzene which upon removal of solid phase of silver bromide deposit further precipitate. After leaving a filtered solution for several hours at room temperature it was found that the small amount of dispersed AgBr coagulated and polarimeter readings could be taken but by that time complete racemization had taken place and the solution possessed no optical rotation. These measurements were unsatisfactory because the 2-octyl perchlorate initially formed could have possessed optical activity but subsequently lost it on standing.

2-Octyl perchlorate is readily attacked by nucleophilic anions. By using bromide ions it is possible to carry through a cycle which regenerates 60% of the 2-octyl bromide.

(16) H. Burton and D. A. Munday, *J. Am. Chem. Soc.*, **79**, 1718 (1957).

$$\text{C}_8\text{H}_{17}\text{Br} \left.\begin{array}{c} \\ + \\ \text{AgClO}_4 \end{array}\right\} \begin{array}{l} \xrightarrow{60-61\%} \text{C}_8\text{H}_{17}\text{OClO}_3 \xrightarrow{\text{Br}^-} \text{C}_8\text{H}_{17}\text{Br} \\ \\ \xrightarrow{38-39\%} \text{olefin} + \text{HClO}_4 \xrightarrow{\text{Br}^-} \text{olefin} + \text{ClO}_4^- + \text{HBr}_2^- \end{array}$$

The extent of silver bromide production was determined by potentiometric titration in the usual manner. Samples removed for measurement of optical rotation were introduced into an equal volume of a 0.25 M solution of tetraethylammonium bromide in acetonitrile, and after filtration the rotation of the (+)-2-octyl bromide present was measured in the 1:1 acetonitrile–benzene mixture. A control experiment showed that a 0.147 M solution of (+)-2-octyl bromide in 1:1 acetonitrile–benzene saturated with tetraethylammonium bromide was only 10% racemized after 10 hr. at room temperature. Since the optical rotations were measured immediately after mixing, the relatively slow racemization of the (+)-2-octyl bromide can be neglected. During the first 30 min. of reaction the mean value for the retention of optical purity, Z, in the (−)-2-octyl perchlorate is 58% (Table VIIA), but on standing for 180 min. a significant amount of racemization occurred, consistent with our previous finding of complete racemization when 2-octyl perchlorate was left

standing in benzene for several hours at room temperature. A more detailed investigation of the rate of racemization of (−)-2-octyl perchlorate is presented in Table VIIB.

The presence of tetra-*n*-butylammonium perchlorate in the original reaction mixture has no effect upon the resulting retention of optical purity in the (+)-2-octyl bromide formed from the (−)-2-octyl perchlorate (Table VIIC). Consequently, the degree of retention of optical purity, when the cycle (+)-$C_8H_{17}Br$ $\xrightarrow[\text{Et}_4\text{NBr}]{\text{AgClO}_4}$ (−)-$C_8H_{17}OClO_3$ $\xrightarrow[\text{2nd stage}]{}$ (+)-$C_8H_{17}Br$ is carried through is about 60% irrespective of whether or not additional perchlorate ions are present in the first stage.

If the second stage is assumed to be a nucleophilic attack by bromide ions on 2-octyl perchlorate *via* an SN2 mechanism, taking place with 100% retention of optical purity in the inversion, then we can say that under the reaction conditions the silver perchlorate converts the (+)-2-octyl bromide into (−)-2-octyl perchlorate with 60% retention of optical purity in the inversion. If 100% retention of optical purity in the inversion by the bromide ion attack is not assumed, then the 60% retention of optical purity in attack by silver perchlorate on (+)-2-octyl bromide must be regarded as a lower limit to the possible value.

Discussion

The reaction between silver perchlorate and 2-octyl bromide in benzene differs from that in acetonitrile in that the order in silver perchlorate for low concentrations approaches a limiting value of 1.5 and not 1.0 as in acetonitrile.[7] It also proceeds much faster in benzene; this is not surprising in view of the fact that CH_3CN has a higher affinity for Ag^+ forming the more stable $Ag(NCCH_3)_2{}^+$ complex, with the two Ag ligand bonds lying colinearly. As the stability of the Ag^+ complex increases its electrophilic capacity is progressively reduced. Further, the products in benzene are essentially a mixture of olefins and *2-octyl perchlorate*. The observed accelerative effect when tetra-*n*-butylammonium perchlorate is added to a fixed concentration of 2-octyl bromide and of silver perchlorate is such that very small concentrations cause a marked acceleration. However, added tetra-*n*-butylammonium perchlorate soon produces a maximum velocity increase and addition of further tetra-*n*-butylammonium perchlorate has little effect upon the reaction velocity.
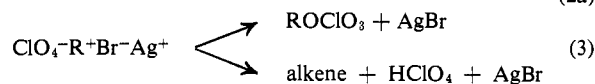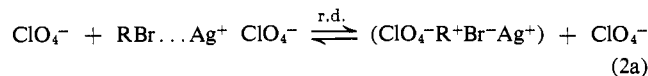
The ratio of substitution to elimination is a constant independent of the concentration of reactants and independent of the concentration of added tetra-*n*-butylammonium perchlorate. The (−)-2-octyl perchlorate is formed from (+)-2-octyl bromide and $AgClO_4$ in benzene at 25.0° with 60% retention of optical purity in the inversion irrespective of the silver perchlorate concentration or whether tetra-*n*-butylammonium perchlorate is added.

All these observations can be explained in terms of quadruple ion intermediates ($ClO_4{}^-R^+Br^-Ag^+$) as suggested for the reaction in acetonitrile solution,[1,5-7] but account being taken of the fact that in benzene, electrostatic forces extend over much greater distances.[17]
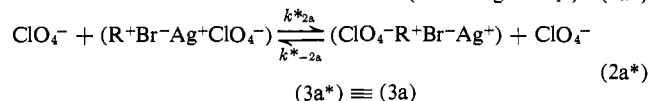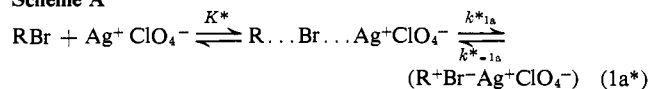
(17) Two ions of unit charge in benzene have a mutual electrostatic energy equal to the mean kinetic energy of either alone a line at a separation which corresponds to a statistical distribution at a salt concentra-

A priori, it would appear that the 1.5 order at low [AgClO₄] might be ascribed to an activated complex whose *limiting* stoichiometric composition is $ClO_4{}^-$, RBr, $Ag^+ClO_4{}^-$. Actually, as the salt concentration is increased it is also accompanied by the formation of higher ionic aggregates carrying no *net* charge so that if in the presence of such aggregates the stoichiometric composition of the activated complex were still $ClO_4{}^-$, RBr, $Ag^+ClO_4{}^-$ then the slope of the logarithmic plot should, as ion pairs became replaced by quadruple ions, fall from 1.5 to 0.75. The kinetic orders found at higher concentrations ($>10^{-3}$ M) would then have to be ascribed to the incursion of reaction components having the stoichiometric composition: $ClO_4{}^-$, RBr, $(Ag^+ClO_4{}^-)_n$ in which *n* increases ($n = 2, 3...$) as [AgClO₄] is increased (Scheme A). Increased aggregation could on balance lead to an increase in rate provided the electrophilic capacity of the silver perchlorate aggregates more than counterbalances the reduction in the number of entities present. *However, the concentration of free perchlorate ions is exceedingly low and the the rate coefficient leading to the formation of ($ClO_4{}^-R^+Br^-Ag^+$) quadruple ions must be of the order of a diffusion-controlled process.* This can only be so provided Scheme A is amplified (see Scheme A*) to contain step 1a* (the electrophilically assisted bond heterolysis of the RBr...$Ag^+ClO_4{}^-$ complex to produce $R^+Br^-Ag^+ClO_4{}^-$) followed by step 2a* (the attack by $ClO_4{}^-$ on $R^+Br^-Ag^+ClO_4{}^-$ which may indeed be diffusion controlled). But even on this amplified scheme it is necessary to assume that $k^*{}_{2a}[ClO_4{}^-]$ and $k^*{}_{-1a}$ are of a similar order of magnitude in order to allow for the observed maximum rate increase by added *n*-Bu₄NClO₄.

Scheme A

$$RBr + Ag^+ClO_4{}^- \rightleftharpoons RBr...Ag^+ClO_4{}^- \quad (1a)$$

$$ClO_4{}^- + RBr...Ag^+\ ClO_4{}^- \xrightarrow{\text{r.d.}} (ClO_4{}^-R^+Br^-Ag^+) + ClO_4{}^- \quad (2a)$$

$$ClO_4{}^-R^+Br^-Ag^+ \begin{cases} \nearrow ROClO_3 + AgBr \\ \searrow \text{alkene} + HClO_4 + AgBr \end{cases} \quad (3)$$

Scheme A*

$$RBr + Ag^+\ ClO_4{}^- \underset{}{\overset{K^*}{\rightleftharpoons}} R...Br...Ag^+ClO_4{}^- \underset{k^*{}_{-1a}}{\overset{k^*{}_{1a}}{\rightleftharpoons}} (R^+Br^-Ag^+ClO_4{}^-) \quad (1a^*)$$

$$ClO_4{}^- + (R^+Br^-Ag^+ClO_4{}^-) \underset{k^*{}_{-2a}}{\overset{k^*{}_{2a}}{\rightleftharpoons}} (ClO_4{}^-R^+Br^-Ag^+) + ClO_4{}^- \quad (2a^*)$$

$$(3a^*) \equiv (3a)$$

tion of about 10^{-5} M. From well below this concentration to a long way above it most of the ions associate into pairs or other groups of shorter range. By Bjerrum's definition,[18] for univalent ions in benzene, the maximum length of an ion pair is about 120 Å., though shorter pairs are of course much more prevalent. These ideas have been extended by Fuoss and Kraus[19] who have shown that in solvents of low dielectric simple ions will associate with pairs to form triple ions. Since they carry a *net* charge, triple ions, like simple ions, appear only in very low concentration in benzene. The next stage of association is the one in which the net charge is lost in the formation of coupled pairs or quadruple ions. At low concentrations of AgClO₄ in benzene ion pairs predominate but as the concentration of salt increases quadruple ions and higher ionic aggregates carrying no *net* charge are present in appreciable proportions.[20]
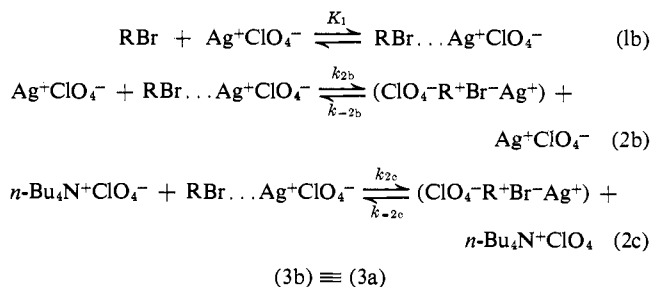
(18) N. Bjerrum, *Kgl. Danske Videnskab. Selskab Mat. Fys. Medd.*, **7** No. 9 (1926).

(19) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387, 3614 (1933); **57**, 1 (1935); *cf.* also R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. (Publisher) Ltd., London, 1955, p. 390.
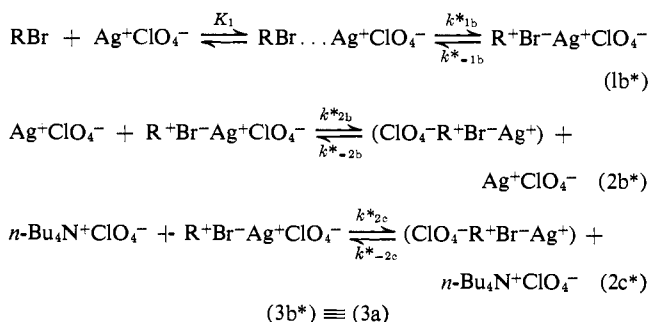
(20) F. M. Battson and C. A. Kraus, *J. Am. Chem. Soc.*, **56**, 2017 (1934).

Conductivity indicates that in a 0.001 M solution of silver perchlorate in benzene the concentration of free ions is negligibly small[19] ($[Ag^+] \simeq [ClO_4^-] \approx 10^{-12}\ M$); consequently the abundant ion pairs and aggregates of ion pairs would be expected *a priori* to be, not only the actual electrophilic catalysts, but also the nucleophilic promoters of the ionization process (Scheme B) or of the quadruple-ion rearrangement[13] (Scheme B*).

Scheme B

$$RBr\ +\ Ag^+ClO_4^- \xrightleftharpoons{K_1} RBr\ldots Ag^+ClO_4^- \qquad (1b)$$

$$Ag^+ClO_4^-\ +\ RBr\ldots Ag^+ClO_4^- \xrightleftharpoons[k_{-2b}]{k_{2b}} (ClO_4^-R^+Br^-Ag^+)\ +$$
$$Ag^+ClO_4^- \qquad (2b)$$

$$n\text{-}Bu_4N^+ClO_4^-\ +\ RBr\ldots Ag^+ClO_4^- \xrightleftharpoons[k_{-2c}]{k_{2c}} (ClO_4^-R^+Br^-Ag^+)\ +$$
$$n\text{-}Bu_4N^+ClO_4 \qquad (2c)$$

$$(3b) \equiv (3a)$$

Scheme B*

$$RBr\ +\ Ag^+ClO_4^- \xrightleftharpoons{K_1} RBr\ldots Ag^+ClO_4^- \xrightleftharpoons[k^*_{-1b}]{k^*_{1b}} R^+Br^-Ag^+ClO_4^-$$
$$(1b^*)$$

$$Ag^+ClO_4^-\ +\ R^+Br^-Ag^+ClO_4^- \xrightleftharpoons[k^*_{-2b}]{k^*_{2b}} (ClO_4^-R^+Br^-Ag^+)\ +$$
$$Ag^+ClO_4^- \qquad (2b^*)$$

$$n\text{-}Bu_4N^+ClO_4^-\ +\ R^+Br^-Ag^+ClO_4^- \xrightleftharpoons[k^*_{-2c}]{k^*_{2c}} (ClO_4^-R^+Br^-Ag^+)\ +$$
$$n\text{-}Bu_4N^+ClO_4^- \qquad (2c^*)$$

$$(3b^*) \equiv (3a)$$

A close examination of the cryoscopic data in benzene[20] indicates that already at 0.001 M a significant proportion of the silver perchlorate is in the quadruple ion from and that as the concentration of salt increases from 0.001 to 0.01 M, progressively increasing numbers of ion pairs become coupled to produce quadruple ions (and possibly higher aggregates). It would thus appear that a kinetic order of 1.5 in silver perchlorate in this region should be correlated with a reaction mechanism whose activated complex has the stoichiometric composition RBr, $n(Ag^+ClO_4^-)$ in which the *limiting* value of n is 2 (Schemes B and B*) and in which the value of n increases ($n = 2, 3, 4$, etc.) as the concentration of silver perchlorate rises. The increased aggregation of silver perchlorate could on balance lead to an increase in rate (and hence to a slow rise in the "apparent" kinetic order) provided the electrophilic capacity of the aggregate more than counterbalances the reduction in the number of catalytic entities present. Actually the 2-octyl bromide–silver perchlorate complex would probably be more accurately represented by eq. 1 where m

$$RBr\ +\ (Ag^+ClO_4^-)_m \xrightleftharpoons{K_m} RBr\ldots (Ag^+ClO_4^-)_m \rightleftharpoons$$
$$R^+\ Br^-(Ag^+ClO_4^-)_m \qquad (1)$$

$= 1, 2, 3$, etc., with Schemes B and B* given above as simplifications of more general schemes which would take into account the association of $Ag^+ClO_4^-$ and $n\text{-}Bu_4N^+ClO_4^-$ ion pairs to quadruple ions and higher aggregates. Schemes B and B* represent mechanisms in which the attacking nucleophiles (steps 2b, 2b*, 2c, and 2c*) are ion pairs. The central point in our interpretation is that the abnormally high ratios $[Ag^+ClO_4^-]/[ClO_4^-]$ and $[n\text{-}Bu_4N^+ClO_4^-]/[ClO_4^-]$ should

overwhelmingly favor steps 2 in Schemes B and B* over those in Schemes A and A* even though the free ClO_4^- might be considerably more nucleophilic towards the complex. The fact that at low concentrations of silver perchlorate, the addition of very small amounts of tetra-n-butylammonium perchlorate is sufficient to catalyze strongly the reaction is not uniquely consistent with Scheme A* but can be explained on Schemes B and B* as well, provided the perchlorate ion in the n-$Bu_4N^+ClO_4^-$ ion pair is assumed to be a significantly stronger nucleophilic promoter than in the $Ag^+ClO_4^-$ ion pair, *i.e.*, provided $k_{2c} > k_{2b}$ or $k^*_{2c} > k^*_{2b}$. This assumption finds strong support in conductivity data[9] which show that on a statistical basis the ionic partners in silver perchlorate ion pair ($K_d = 0.0078 \times 10^{-18}$) are much more tightly held than those in tetra-n-butylammonium perchlorate ion pair ($K_d = 2.9 \times 10^{-18}$). We have also a precedent for assuming that X^- in $R_4N^+X^-$ ion pair is a stronger nucleophile than X^- in Ag^+X^- ion pair from our studies of the reaction of nitrite salts with 2-octyl bromide in acetonitrile.[7]

The observations of a maximum rate enhancement upon the addition of tetra-n-butylammonium perchlorate, as well as the fact that the magnitude of this catalysis diminishes with increasing concentration of silver perchlorate, rule out Scheme B. On the other hand Scheme B* provides a satisfactory explanation of all our observations. In contrast to Scheme A* which required an abnormally large value for k^*_{2a} in order to account for the observed experimental reaction rate Scheme B* leads to reasonable values for both k^*_{2b} and k^*_{2c}. Using the generalized Scheme B* which includes the equilibrium constant K_m in place of K_1 (see above) and applying a steady-state treatment with respect to $[R^+Br^-(Ag^+ClO_4^-)_m]$, assuming that all $[ClO_4^-R^+Br^-Ag^+]$ intermediates collapse to give products by a fast step (3b*), one obtains eq. 2.

$$\frac{d[AgBr]}{dt} = k^*_{1b}[RBr\ldots(Ag^+ClO_4^-)_m] \times$$
$$\frac{k^*_{2b}[Ag^+ClO_4^-]\ +\ k^*_{2c}[n\text{-}Bu_4N^+ClO_4^-]}{k^*_{-1b}\ +\ k^*_{2b}\ [Ag^+ClO_4^-]\ +\ k^*_{2c}\ [n\text{-}Bu_4N^+ClO_4^-]}$$
$$(2)$$

(i) At low $[AgClO_4]$ in the absence of n-Bu_4NClO_4 one obtains eq. 3. It will be noted that as the concentration of silver perchlorate is decreased, the value of

$$\frac{d[AgBr]}{dt} = \frac{k^*_{1b}k^*_{2b}[RBr\ldots(Ag^+ClO_4^-)_m][Ag^+ClO_4^-]}{k^*_{-1b}\ +\ k^*_{2b}\ [Ag^+ClO_4^-]}$$
$$(3)$$

m will tend towards unity and $k^*_{-1b} > k^*_{2b}[Ag^+ClO_4^-]$ leading to RBr, $2(Ag^+ClO_4^-)$ as the limiting stoichiometric composition of the activated complex.

(ii) In the presence of added n-Bu_4NClO_4 (at low $[AgClO_4]$) or at relatively high concentration of silver perchlorate alone conditions may be reached such that the inequality $k^*_{2b}[Ag^+ClO_4^-]\ +\ k^*_{2c}[n\text{-}Bu_4N^+ClO_4^-] > k^*_{-1b}$ holds, so that k^*_{1b} becomes rate determining leading to eq. 4 where $[RBr\ldots(Ag^+ClO_4^-)_m] =$

$$\frac{d[AgBr]}{dt} = k^*_{1b}[RBr\ldots(Ag^+ClO_4^-)_m] \qquad (4)$$

$[RBr][(Ag^+ClO_4^-)_m]/K_m$ with $m = 1, 2, 3$, etc.

Optical results indicate that stages 2b* and 2c* cannot be regarded as leading directly to covalent perchlorate (*i.e.*, not S$_N$2 Ag$^+$) and give further justification for postulating a quadruple ion intermediate in these anion-assisted silver ion reactions. It can be postulated that the quadruple ion intermediate is such that *ca.* 40% racemization can occur within it prior to combination to yield inverted 2-octyl perchlorate ester. Immediate collapse of a rigidly oriented quadruple ion would be expected to yield 100% inversion in configuration.

The nonvariance of the product ratio over a wide range of added tetra-*n*-butylammonium perchlorate concentration and the production of 2-octyl perchlorate ester possessing optical activity but which racemizes on standing both indicate that the product partitioning steps are subject to kinetic and not thermodynamic control.

Experimental Section

Materials were prepared and purified as previously described,[1,5–7] with the exception of the acetonitrile used to quench the reaction. Commercial acetonitrile even after drying was not sufficiently pure for this purpose, precipitating significant amounts of silver ion from solution. By chromatographing over activated alumina these impurities were reduced to a very low concentration which did not affect our studies involving CH$_3$CN as a quenching medium. Acetonitrile used in the kinetic determination of the stability of 2-octyl perchlorate in acetonitrile–benzene mixtures was purified as described before.[5,7]

Benzene of "AnalaR" quality was dried by boiling it for 1 day with, and then fractionating it from, molten potassium.[21] We found this material to be just as good as that prepared with the aid of the more recently suggested drying agent, calcium hydride.

Tetra-*n*-butylammonium perchlorate was prepared, purified, and dried as described in an earlier investigation.[22]

Determination of Over-all Rate of Reaction. Samples were introduced into excess of acetonitrile, to quench the reaction, and subsequently titrated potentiometrically in acetone containing a little nitric acid against standard aqueous potassium chloride solution, using a silver wire electrode and potassium nitrate–agar bridge to a dip-type calomel reference electrode. After introduction into the acetonitrile samples could be kept

for several hours with no change in the concentration of silver ion in solution.

Determination of the Percentage of Reaction with Acid Formation. Samples were introduced into an excess of a neutral solution of lithium chloride in acetone. The lithium chloride prevented further reaction by precipitation of silver ions from solution *and it also destroyed any 2-octyl perchlorate without concurrent acid formation.* Titration of the acid present was then carried out against a standard solution of sodium methoxide in methanol using lacmoid as indicator. The two variations to the usual manner of destroying the 2-octyl perchlorate are fully described in the treatment of results.

Determination of the Percentage of Reaction with Olefin Formation. Aliquots (5.00 ml.) were added to 5 ml. of a 0.1 *M* solution of lithium chloride in "AnalaR" glacial acetic acid and the silver halide precipitate quickly filtered off at the pump. The solution was washed through with 15 ml. of "AnalaR" glacial acetic acid. Excess of a solution of bromine in acetic acid was added and then solid potassium iodide to liberate a quantity of iodine equal to the excess bromine. This liberated iodine was titrated against standard sodium thiosulfate solution. The addition of distilled water and titration using starch as indicator was found to be unsatisfactory due to a small film of benzene containing much of the iodine separating out. A method was developed by which 20 ml. of carbon tetrachloride, followed by 50 ml. of water, was added and back titration against standard sodium thiosulfate was carried out until the lower carbon tetrachloride layer was colorless. It was found that the benzene as purified contained trace amounts of olefin to which bromine addition took place. Blank experiments showed that the concentration of such olefin varied from sample to sample but the concentration with respect to bromine addition was usually in the region of 0.003 *N*. Since measurements were related to the kinetic zero reading this did not affect the measurement of olefin formation during the reaction.

Optical Studies. The (−)-2-octyl perchlorate formed was reconverted into (+)-2-octyl bromide by the introduction of 5.00-ml. reaction aliquots into 5.00 ml. of a solution 0.25 *M* in tetraethylammonium bromide in acetonitrile. The solution was filtered from precipitated silver bromide and tetraethylammonium bromide, whose solubility in 50% acetonitrile–benzene is exceeded. The optical rotation of the solution was measured in a 2-dm. polarimeter tube at room temperature.

(21) E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).
(22) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai, and Y. Pocker, *ibid.*, 1220 (1957).