in the A_{H_β} values of the other nitroxides in Table I.

(28) J. J. Zeilstra and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **92**, 954 (1973).

(29) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(30) The determination of rotamer ratios at temperatures around −40° is seriously hampered by viscosity broadening of the signals due to both rotamers.

(31) The proposed electron transfer process has been criticized by Beckwith and Lawton; see ref 9b.

(32) The reduced average A_{H_β} of **27** compared with that of $C_2H_5N(—O)—O—C_4H_7O$ (C_4H_7O = 2-tetrahydrofuryl; A_{H_β} = 8.08 G[9b]) agrees with this view.

(33) N. Kornblum, S. D. Boyd, and N. Ono, *J. Am. Chem. Soc.*, **96**, 2580 (1974).

(34) Compare: L. Jonkman, H. Muller, and J. Kommandeur, *J. Am. Chem. Soc.*, **93**, 5833 (1971).

(35) Simple alkyl alkoxy nitroxides are known to decay into the corresponding nitroso alkanes and alkyl nitrites. Fragmentation involving C–O bond fission is relatively unimportant. See Perkins and Roberts, ref 9a.

(36) J. J. Zeilstra and J. B. F. N. Engberts, *Tetrahedron*, **29**, 4299 (1973).

(37) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).

(38) W. E. Truce, T. C. Klingler, J. E. Paar, H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).

(39) W. V. Farrar, *J. Chem. Soc.*, 904 (1964).

Electrophilic Catalysis in Nucleophilic Substitution and Elimination. VII. Kinetics and Mechanism of Reaction of Neopentyl Iodide with Tetraethylammonium and Silver Nitrates and Perchlorates in Acetonitrile[1]

Y. Pocker* and Wah-Hun Wong

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98195. *Received September 5, 1974*

Abstract: The kinetics of the reaction of neopentyl iodide with $AgNO_3$ and $AgClO_4$ with and without added tetraethylammonium nitrate and perchlorate has been investigated in detail in acetonitrile at 75.0° and found to exhibit a general kinetic pattern represented by $V_i = k_2°[RI][Ag^+] + k_3^{Y^-}[RI][Ag^+][Y^-]$. The rate enhancements by added Et_4NNO_3 and Et_4NClO_4 were indicative of anionic assistance in the rate-determining step. The olefin proportions of the products have also been determined and strongly suggest that *tert*-amyl cations are reaction intermediates both in the absence and presence of anionic assistance. The proposed mechanistic scheme involves the rapid formation of an alkyl halide-Ag^+ complex $[RI\ldots Ag]^+$. The subsequent reaction of the complex is rate determining. At moderate salt concentrations, anionic assistance (i.e., intervention by NO_3^- or ClO_4^-) is shown to occur within this slow step. However, at low salt concentrations, <0.01 *M*, the decomposition of the complex involves only CH_3CN participation in the rate-controlling step.

Silver salt catalysis of simple primary and secondary alkyl halides and allyl halides has been investigated somewhat extensively.[1-16] The kinetic studies of these reactions with various silver salts in a variety of solvents have been found to exhibit a complex dependence on silver salt concentration.[1-4,8-13] With $AgNO_3$, the counterion (NO_3^-) being relatively nucleophilic, the overall kinetic order approximates 2.5, first order in alkyl halide, first order in stoichiometric silver ion, and one-half order in stoichiometric nitrate ion.[3] However, if the reasonably nucleophilic NO_3^- is replaced by the weakly nucleophilic ClO_4^-, the reaction is first order in alkyl halide, 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*.[3] In several cases, anionic participation[1-4,6,8] or, in cases when the counterions were weakly nucleophilic, solvent participation[3,14] was concurrent with electrophilic assistance by Ag^+ in the rate-determining step.

The proposed mechanistic scheme (Scheme I) for $AgNO_3$ and $AgClO_4$ catalysis involves the formation of an alkyl halide-Ag^+ complex.[5,16] The subsequent decomposition of this complex is rate determining, with anionic assistance (i.e., intervention by NO_3^- or ClO_4^-) within this slow step.[1-4,6]

Scheme I

$$RI + Ag^+ \rightleftharpoons (RI\ldots Ag)^+$$

$$Y^- + (RI\ldots Ag)^+ \xrightarrow{\text{rd}} (Y^-R^+I^-Ag^+)$$

$$(Y^-R^+I^-Ag^+) \begin{array}{l} \nearrow\ RY + AgI \\ \searrow\ \text{alkenes} + HY + AgI \end{array}$$

$$Y^- = NO_3^- \text{ or } ClO_4^-$$

Previous kinetic[1-4,8-13] and stereochemical[3,6,7,13,18] studies have revealed that these electrophilically catalyzed reactions do not proceed by a simple carbonium ion, or strictly SN1 mechanism. Instead, these reactions may be termed Y^--SN1-Ag^+ (in the Hughes-Ingold terminology[13]), in order to account for the fact that, in some instances, rearranged products are isolated,[15,19-21] and, at the same time, an almost complete inversion of optical configuration occurs in the direct substitution products.[3,6,13,18] The stereochemical studies made recently by Cohen and Solash showed that, in the Ag^+-assisted solvolysis of *trans,trans*-2-bromodecalin in acetonitrile with $AgClO_4$, the reaction occurs with overwhelming retention of configuration.[7] It was suggested that the ClO_4^- may be present at the back providing steric hindrance to solvent attack and that the developing carbonium ion undergoes a front side Ritter reaction[17] with CH_3CN. It is interesting to note that, despite the low nucleophilicity of ClO_4^-, its stabilization of the incipient carbonium ion cannot be overlooked. It is also significant to note that, when the anionic reagent is a weak nucleophile, solvent (CH_3CN) intervention is operative since products derived from alkylation of CH_3CN by carbonium ions are known to arise.[6c,17] Additional evidence for some anion par-

Table I. Initial Velocities (V_i) and Rate Coefficients for AgI Production in the Reaction of Neopentyl Iodide with $AgNO_3$ in CH_3CN at 75.0°

$[AgNO_3]$, M	[RI], M	α[a]	$10^7 V_i$,[b] $M\ sec^{-1}$	$10^3 k_2$,[c] $M^{-1}\ sec^{-1}$	$10^3 k_{2.5}$,[d] $M^{-1.5}\ sec^{-1}$	$10^3 k_3$, $M^{-2}\ sec^{-1}$	$10^3 k$,[e] $M^{-1}\ sec^{-1}$	$10^3 k_3^{NO_3^-}$, $M^{-2}\ sec^{-1}$
0.0030	0.0120	0.94	0.0151	0.042	0.767	14	0.0091	3.43
0.0060	0.0120	0.91	0.0346	0.048	0.619	8	0.016	3.25
0.0120	0.0120	0.79	0.0763	0.053	0.484	4.42	0.0253	3.38
0.0243	0.0243	0.72	0.39	0.066	0.425	2.72	0.041	3.24
0.0311	0.0250	0.71	0.62	0.080	0.457	2.58	0.055	3.51
0.0310	0.0506	0.71	1.29	0.082	0.466	2.64	0.057	3.65
0.0396	0.0505	0.68	1.68	0.084	0.422	2.21	0.060	3.28
0.0485	0.0488	0.65	2.20	0.093	0.430	1.98	0.070	3.44
0.0500	0.0484	0.65	2.28	0.094	0.425	1.90	0.071	3.37
0.0502	0.0448	0.65	2.07	0.092	0.400	1.85	0.069	3.26
0.0613	0.0492	0.62	3.13	0.106	0.440	1.66	0.084	3.58
0.0628	0.0510	0.62	3.38	0.105	0.420	1.66	0.083	3.45
0.0753	0.0247	0.58	2.27	0.122	0.450	1.63	0.102	4.02
0.1280	0.0228	0.53	5.20	0.178	0.512	1.47	0.159	4.40
0.1273	0.0457	0.53	10.60	0.181	0.522	1.51	0.162	4.55
0.1523	0.0500	0.51	16.80	0.220	0.595	1.43	0.202	5.11
0.2550	0.0453	0.46	47.00	0.406	0.806	1.60	0.390	7.21
0.4048	0.0479	0.45	135.0	0.696	1.06	1.71	0.680	8.31
0.4917	0.0500	0.44	220.0	0.893	1.23	1.80	0.878	9.16
0.6020	0.0500	0.43	354.0	1.18	1.50	1.93	1.17	10.50

[a] α = degree of dissociation of $AgNO_3$ (ref 22). [b] $V_i = k_2\,[RI]\,[AgNO_3]_s$. [c] The coefficients k_2 were calculated from second-order rate plots and also from the integrated expression given in footnote b. [d] The 2.5-order coefficients were calculated from the integrated expressions given in ref 3. [e] $k = (k_2 - \alpha k_2^\circ)$ where $k_2^\circ = 0.035 \times 10^{-3} M^{-1}\ sec^{-1}$.

ticipation in the rate-controlling step comes from a brief investigation in which it was observed that the sterically hindered neopentyl iodide reacted much slower than the less hindered ethyl iodide.[2]

At present we believe that there is still a lack of understanding as to the detailed mechanism of these silver salt catalyzed reactions. Therefore, in an attempt to further resolve the problem, we have chosen to study in greater detail the action of various silver salts on neopentyl iodide. It proved advantageous to vary the nucleophilic capacity of the anion while retaining the same substrate and solvent. Our choice of substrate is quite apparent since neopentyl compounds under solvolytic conditions react strictly via the SN1 mechanism, minimizing, as a consequence of steric hindrance, the possibility of any bimolecular substitution (SN2) reaction.[15,19-21] Our aim in this investigation was twofold, namely (1) to delineate the mechanism of silver salt catalysis and (2) to provide additional information about ionization–rearrangement processes in neopentyl derivatives.[15,19-21]

Results

Kinetic Results. The reaction of neopentyl iodide with Et_4NNO_3 in acetonitrile, as determined by iodide ion production, has been found to be extremely slow. At 75.0°, a solution 0.0897 M in neopentyl iodide and 0.100 M in Et_4NNO_3 reacted to the extent of 1.9% of the neopentyl iodide after 6 days. The reaction with $AgNO_3$ and $AgClO_4$, however, is very much faster, although $AgNO_3$ caused greater rate enhancement than the corresponding $AgClO_4$ reaction. Reactions of neopentyl iodide with $AgNO_3$ and $AgClO_4$, whose concentrations range from 0.003 to 0.60 and 0.003 to 0.40 M, respectively, have been thoroughly investigated at 75.0°. The analytical treatment of the results of the reaction of neopentyl iodide with $AgNO_3$ and $AgClO_4$ was first in terms of the 2.5 order originally used by Pocker and Kevill[3] for reactions of *sec*-alkyl halides with silver nitrates. The treatment was reasonably successful (Tables I and II). However, a more searching analysis of the results obtained in the presence of added tetraethylammonium salts indicated that the reactions of neopentyl iodide with silver salts exhibit a more complicated behavior. Nevertheless, the first-order dependency in neopentyl iodide was formally documented for a given $AgClO_4$ concentration while varying the concentration of neopentyl iodide ninefold (Table III).

Treatment of the data using a combination of second- and third-order terms leads to a more consistent kinetic scheme. It was found that the initial velocities (V_i) of the Ag^+-assisted reactions follow the rate expression eq 1

$$V_i = \alpha k_2^\circ [RI][AgY]_s + \alpha^2 k_3^{Y^-} [RI][AgY]_s^2 \qquad (1)$$

where α = degree of dissociation of AgY ($AgNO_3$ or $AgClO_4$) in acetonitrile;[22,23] k_2° = second-order rate coefficient for Ag^+-catalyzed reaction unassisted by the counterions, NO_3^- or ClO_4^-; $k_3^{Y^-}$ = third-order rate coefficient for Ag^+-catalyzed reaction, assisted by counterion Y^- (e.g., NO_3^- or ClO_4^-); $[AgY]_s$ = stoichiometric $AgNO_3$ or $AgClO_4$ concentration, in moles/liter.

The second-order rate constant associated with Ag^+ catalysis, $k_2^\circ = 0.035 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 75.0°, is obtained by extrapolation to zero NO_3^- or ClO_4^- concentration as shown in Figure 1 and is valid for all the dissociated silver salts irrespective of their conjugate anions (NO_3^- or ClO_4^-). Thus, at any given temperature in CH_3CN, k_2° varies only with the type of alkyl halide used.

Using the values of the observed second-order rate coefficients (k_2) and assuming Janz's values for the degree of $AgNO_3$ and $AgClO_4$ dissociation,[22] the third-order rate constants for NO_3^-- and ClO_4^--assisted reactions, $k_3^{NO_3^-}$ and $k_3^{ClO_4^-}$, respectively, have been calculated using eq 2.

$$k_3^{Y^-} = \frac{(k_2 - \alpha k_2^\circ)}{(\alpha^2 [AgY]_s)} \qquad (2)$$

Tables I and II summarize the results of these computations and show that, in reasonably dilute solutions, $k_3^{NO_3^-}$ and $k_3^{ClO_4^-}$ remain essentially constant. Thus, up to $[AgNO_3]$ = 0.0628 M and $[AgClO_4]$ = 0.0590 M, the mean values of $k_3^{NO_3^-}$ and $k_3^{ClO_4^-}$ are 3.42×10^{-3} and $1.40 \times 10^{-3}\ M^{-2}\ sec^{-1}$, respectively. However, above 0.063 M silver salt, these rate constants rise with increasing salt concentration.

It should also be noted that our kinetic measurements were extended down to 0.0030 M silver salt so as to provide a more thorough test of the two parameter treatment as represented by eq 1. The newly proposed rate expression is

Table II. Initial Velocities (V_i) and Rate Coefficients for AgI Production in the Reaction of Neopentyl Iodide with $AgClO_4$ in CH_3CN at 75.0°

$[AgClO_4]$, M	[RI], M	α[a]	$10^7 V_i$,[b] $M\ sec^{-1}$	$10^3 k_2$,[c] $M^{-1}\ sec^{-1}$	$10^3 k_{2.5}$,[d] $M^{-1.5}\ sec^{-1}$	$10^3 k_3$, $M^{-2}\ sec^{-1}$	$10^3 k$,[e] $M^{-1}\ sec^{-1}$	$10^3 k_3^{ClO_4^-}$, $M^{-2}\ sec^{-1}$
0.0030	0.0120	0.94	0.0132	0.0365	0.666	12.1	0.0036	1.35
0.0060	0.0120	0.91	0.0274	0.038	0.491	6.33	0.0061_5	1.23
0.0120	0.0120	0.79	0.0562	0.039	0.356	3.25	0.0113_5	1.51
0.0237	0.0237	0.720	0.230	0.0410	0.266	1.73	0.0148	1.29
0.0299	0.0507	0.710	0.700	0.0461	0.266	1.54	0.0213	1.41
0.0301	0.0252	0.710	0.349	0.0460	0.265	1.53	0.0212	1.40
0.0402	0.0254	0.680	0.503	0.0491	0.245	1.22	0.0253	1.36
0.0396	0.0505	0.680	0.966	0.0481	0.242	1.21	0.0243	1.33
0.0473	0.0493	0.655	1.11	0.0495	0.228	1.05	0.0266	1.31
0.0494	0.0494	0.650	1.23	0.0503	0.226	1.02	0.0275	1.32
0.0596	0.0253	0.625	0.886	0.0587	0.243	0.985	0.0368	1.58
0.0590	0.0504	0.625	1.74	0.0585	0.243	0.992	0.0366	1.59
0.1102	0.0234	0.550	2.84	0.102	0.296	0.856	0.0831	2.38
0.1186	0.0470	0.540	5.62	0.101	0.294	0.854	0.0821	2.37
0.1505	0.0484	0.510	8.60	0.118	0.306	0.785	0.100	2.56
0.2395	0.0236	0.465	12.2	0.216	0.451	0.900	0.199	3.84
0.2393	0.0477	0.468	23.6	0.206	0.420	0.856	0.190	3.66
0.4028	0.0495	0.450	74.5	0.375	0.592	0.931	0.359	4.41

[a] α = degree of dissociation of $AgClO_4$ in CH_3CN (ref 22). [b] $V_i = k_2[RI][AgClO_4]_s$. [c] The coefficients k_2 were calculated from second-order rate plots and also from the integrated expressions given in footnote b. [d] The 2.5-order coefficients were calculated from the integrated expressions given in ref 3. [e] $k = (k_2 - \alpha k_2^\circ)$ where $k_2^\circ = 0.035 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

Table III. Initial Velocities and Rate Coefficients for AgI Production in the Reaction of Neopentyl Iodide with $AgClO_4$ in CH_3CN at 75.0°

[Neop-I], M	$[AgClO_4]$, M	$10^7 V_i$, $M\ sec^{-1}$	$10^3 k_1$,[a] sec^{-1}	$10^3 k_2$,[b] $M^{-1}\ sec^{-1}$
0.0473	0.0473	1.11	0.00234	0.0495
0.1507	0.0478	3.71	0.00774	0.0514
0.2841	0.0459	6.52	0.0142	0.0500
0.4223	0.0437	9.41	0.0215	0.0510

[a] $k_1 = k_2$ [Neop-I]. [b] Observed second-order rate coefficients.

shown to apply over a 25-fold variation in silver salt concentration, i.e., from 0.0030 to ca. 0.075 M $AgNO_3$ (Table I) and $AgClO_4$ (Table II). Furthermore, not only is the proposed kinetic analysis more amenable to interpretation in terms of mechanism but it also represents, at the low silver salt concentrations ($\leqslant 0.012$ M), an improvement over the 2.5-order treatment used earlier in this series of papers.[3]

The effect of added Et_4NNO_3 and Et_4NClO_4 was to enhance the rate of attack of neopentyl iodide by $AgNO_3$ and $AgClO_4$ (Tables IV and V). For reactions involving addition of a common ion salt, the kinetics were found to be consistent with the rate expression in eq 3

$$V_i = \alpha k_2^\circ[RI][AgY]_s + \alpha k_3^{Y^-}[RI][AgY]_s(\alpha[AgY]_s + \alpha'[Et_4NY]_s) \quad (3)$$

where α and α' are the degrees of dissociation of AgY and Et_4NY, respectively.

The third-order rate constants, $k_3^{Y^-}$, are computed using eq 4

$$k_3^{Y^-} = \frac{(k_2 - \alpha k_2^\circ)}{[\alpha(\alpha[AgY]_s + \alpha'[Et_4NY]_s)]} \quad (4)$$

The $k_3^{NO_3^-}$ rate constants so calculated ($k_3^{NO_3^-} = 3.46 \times 10^{-3}\ M^{-2}\ sec^{-1}$, Table IV) were found to be practically identical with the ones obtained in the absence of added Et_4NNO_3, $k_3^{NO_3^-} = 3.42 \times 10^{-3}\ M^{-2}\ sec^{-1}$. Similarly, the third-order rate constants, $k_3^{ClO_4^-}$, determined for the reactions with added Et_4NClO_4 have an average value of $1.47 \times 10^{-3}\ M^{-2}\ sec^{-1}$ (Table V) which is in good agreement with the value obtained from reactions without added Et_4NClO_4, i.e., $k_3^{ClO_4^-} = 1.40 \times 10^{-3}\ M^{-2}\ sec^{-1}$.

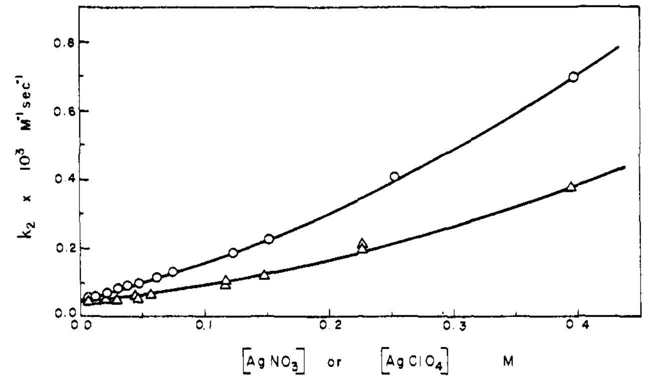


Figure 1. Dependence of the observed second-order rate coefficients, k_2, on silver salt concentration for the reaction of neopentyl iodide with $AgNO_3$ (○) and $AgClO_4$ (△) in CH_3CN at 75.0°.

The introduction of the moderately nucleophilic NO_3^-, in the form of Et_4NNO_3, to the reaction of $AgClO_4$ and neopentyl iodide causes a greater increase in the initial velocity than the corresponding addition of Et_4NClO_4 (Figure 2). However, the reaction velocity increases less than linearly and seems to approach a limiting value upon excessive addition of the salt. A detailed analysis of the data shows that the reaction follows the kinetic expression given in eq 5.

$$V_i = \alpha k_2^\circ[RI][AgClO_4]_s + \alpha^2 k_3^{ClO_4^-}[RI][AgClO_4]_s^2 + \alpha k_3^{NO_3^-}[RI][AgClO_4]_s(\alpha'[Et_4NNO_3]_s) \quad (5)$$

For reactions in which a noncommon ion salt is added, the values of the observed and calculated second-order rate coefficients are reported in Table V. The independently determined constants k_2°, $k_3^{NO_3^-}$, and $k_3^{ClO_4^-}$ were used in the computation of the overall second-order rate coefficient, $k_{2(calcd)}$, eq 6.

$$k_2 = \alpha k_2^\circ + \alpha^2 k_3^{ClO_4^-}[AgClO_4]_s + \alpha k_3^{NO_3^-}(\alpha'[Et_4NNO_3]_s) \quad (6)$$

Clearly, the computed and observed values are in good agreement.

Furthermore, it is interesting to note that the addition of up to 0.25 M tetraethylammonium perchlorate, a salt con-

Table IV. Initial Velocities and Rate Coefficients for AgI Production in the Reaction of $AgNO_3$ with Neopentyl Iodide in the Presence of Et_4NNO_3 in CH_3CN at 75.0°[a]

$[Et_4NNO_3]$, M	α	α'	10^7V_i, $M\ sec^{-1}$	10^3k_2,[d] $M^{-1}\ sec^{-1}$	10^3k,[e] $M^{-1}\ sec^{-1}$	$10^3k_3^{NO_3^-}$,[f] $M^{-2}\ sec^{-1}$
0	0.650[b]	0	2.11	0.093	0.0702	3.44
0.0540	0.500[c]	0.640[b]	2.77	0.118	0.1005	3.40
0.1270	0.405[c]	0.525[b]	3.10	0.132	0.1178	3.38
0.2490	0.310[c]	0.460[b]	3.68	0.157	0.1462	3.62

[a] $[AgNO_3]$ = [neopentyl iodide] = 0.0485 M. [b] Degree of dissociation of $AgNO_3$ (α) and Et_4NNO_3 (α') in CH_3CN (ref 22 and 23). [c] In the presence of added Et_4NNO_3, the degree of dissociation of $AgNO_3$ was calculated using the expression $K_D = (\alpha^2[AgNO_3]_S + \alpha\alpha'[Et_4NNO_3]_S)/(1 - \alpha) = 5.85 \times 10^{-2}\ M$. [d] $V_i = k_2[RI][AgNO_3]_S$. [e] $k = (k_2 - \alpha k_2^\circ)$. [f] Mean $k_3^{NO_3^-} = 3.46 \times 10^{-3}\ M^{-2}\ sec^{-1}$; $k_2^\circ = 0.035 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

Table V. Initial Velocities and Rate Coefficients for AgI Formation in the Reaction of $AgClO_4$ and Neopentyl Iodide with Added Et_4NNO_3 and Et_4NClO_4 in CH_3CN at 75.0°[a]

$[Et_4NClO_4]$, M	$[Et_4NNO_3]$, M	α	α'[b]	10^7V_i, $M\ sec^{-1}$	-10^3k_2,[d] $M^{-1}\ sec^{-1}$	10^3k_2(calcd),[e] $M^{-1}\ sec^{-1}$	10^3k,[f] $M^{-1}\ sec^{-1}$	$10^3k_3^{ClO_4^-}$, $M^{-2}\ sec^{-1}$
0		0.650[b]	0	1.23	0.0503	0.0520	0.0275	1.32
0.0510		0.500[c]	0.640	1.43	0.0588	0.0575	0.0413	1.44
0.1260		0.405[c]	0.525	1.60	0.0655	0.0628	0.0513	1.47
0.2480		0.310[c]	0.460	1.88	0.0772	0.0670	0.0663	1.65
	0.0503	0.500[c]	0.640	2.16	0.0884	0.0908		
	0.1270	0.405[c]	0.525	2.86	0.1175	0.1178		
	0.2490	0.310[c]	0.460	3.37	0.1385	0.1475		

[a] $[AgClO_4]$ = [neopentyl iodide] = 0.0494 M. [b] Degree of dissociation of $AgClO_4$ (α) and Et_4NClO_4 or Et_4NNO_3 (α') in CH_3CN (ref 22 and 23). [c] Calculated using $K_D = 5.85 \times 10^{-2}\ M$ (see footnote c, Table IV). [d] $V_i = k_2[RI][AgClO_4]_S$. [e] Calculated rate constants: $k_2 = \alpha k_2^\circ + \alpha k_3^{ClO_4^-}(\alpha[AgClO_4]_S + \alpha'[Et_4NClO_4]_S)$; $k_2 = \alpha k_2^\circ + \alpha k_3^{NO_3^-}(\alpha'[Et_4NNO_3]_S) + \alpha^2 k_3^{ClO_4^-}[AgClO_4]_S$; $k_2^\circ = 0.035 \times 10^{-3}\ M^{-1}\ sec^{-1}$; $k_3^{NO_3^-} = 3.42 \times 10^{-3}\ M^{-2}\ sec^{-1}$; $k_3^{ClO_4^-} = 1.40 \times 10^{-3}\ M^{-2}\ sec^{-1}$. [f] $k = (k_2 - \alpha k_2^\circ)$.

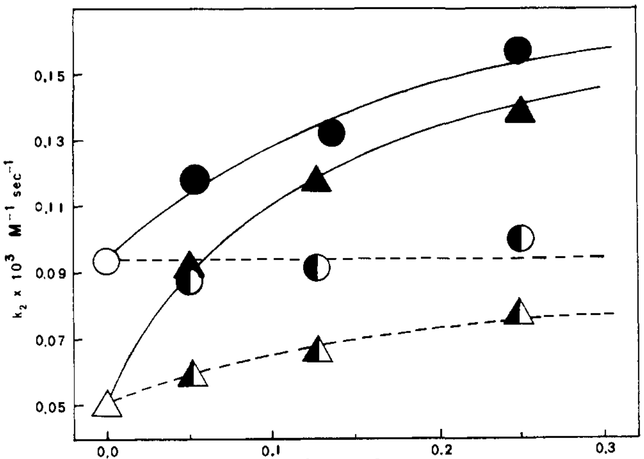


Figure 2. Dependence of the second-order rate coefficients, k_2, on the concentration of Et_4NNO_3 and Et_4NClO_4 in the reaction of neopentyl iodide with $AgNO_3$ (○) and $AgClO_4$ (△) in CH_3CN at 75.0°: $AgNO_3$-Et_4NNO_3 (●) and $AgClO_4$-Et_4NNO_3 (▲), solid lines; $AgNO_3$-Et_4NClO_4 (◐) and $AgClO_4$-Et_4NClO_4 (◭), dotted lines.

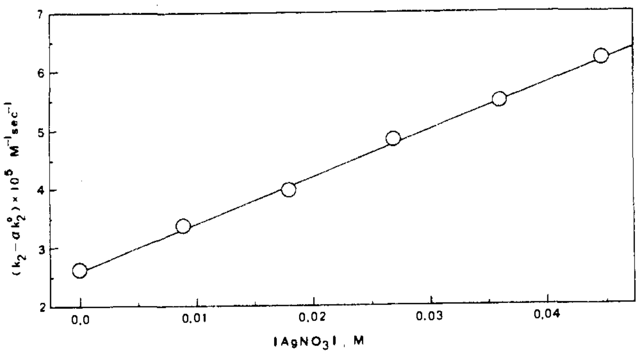


Figure 3. Dependence of $(k_2 - \alpha k_2^\circ)$ on $[AgNO_3]$ for the reaction of neopentyl iodide with $AgNO_3$-$AgClO_4$ mixtures in CH_3CN at 75.0°.

taining the weakly nucleophilic ClO_4^-, to a reaction between neopentyl iodide (0.05 M) and $AgNO_3$ (0.05 M) seems to have little or no effect on the reaction rate, $k_2 = 0.095 \pm 0.005 \times 10^{-3}\ M^{-1}\ sec^{-1}$. Thus the rate enhancements noted in Figure 2 cannot be attributed to significant primary salt effects and are best ascribed as arising from a direct attack by the counterion in the rate-controlling step. This conclusion was tested using mixtures of $AgNO_3$-$AgClO_4$, in which the initial total salt concentration was kept constant while the relative proportions of nitrate and perchlorate salts were varied. In this way, both the total Ag^+ concentration and the ionic strength were held constant at 0.0448 M, while the concentration of the counterionic species (NO_3^- and ClO_4^-) was varied. Indeed, the observed second-order rate coefficients for these reactions have been found to increase linearly with increasing $AgNO_3$ concentration (Table VI, Figure 3).

The newly proposed rate expressions (eq 1 and 3) have also been successfully applied to correlate earlier kinetic data pertaining to the reactions of 2-octyl bromide, with both silver nitrate and silver perchlorate in acetonitrile.[3] For example, at 44.6° with the concentration of silver nitrate varying between 0.0097 and 0.073 M, we obtain $k_2^\circ = 4.4 \times 10^{-6}\ M^{-1}\ sec^{-1}$ and $k_3^{NO_3^-} = 3.71 \times 10^{-2}\ M^{-2}\ sec^{-1}$. At constant silver nitrate concentration (0.0193 M) but with the concentration of tetraethylammonium nitrate varying between 0.0107 and 0.0799 M, we obtain $k_2^\circ = 4.4 \times 10^{-6}\ M^{-1}\ sec^{-1}$ and $k_3^{NO_3^-} = 3.74 \times 10^{-2}\ M^{-2}\ sec^{-1}$. With silver perchlorate at 44.6°, we obtain $k_2^\circ = 4.4 \times 10^{-6}\ M^{-1}\ sec^{-1}$ and $k_3^{ClO_4^-} = 0.23 \times 10^{-3}\ M^{-2}\ sec^{-1}$. At 60°, with the concentration of silver perchlorate varying between 0.0041 and 0.0447 M, we obtain $k_2^\circ = 3.1 \times 10^{-5}\ M^{-1}\ sec^{-1}$ and $k_3^{ClO_4^-} = 1.41 \times 10^{-3}\ M^{-2}\ sec^{-1}$. At constant silver perchlorate concentration (0.0151 M) and with tetraethylammonium perchlorate varying between 0.0146 and 0.117 M, we obtain $k_2^\circ = 3.1 \times 10^{-5}\ M^{-1}\ sec^{-1}$ and $k_3^{ClO_4^-} = 1.32 \times 10^{-3}\ M^{-2}\ sec^{-1}$. In fact, at any given temperature in acetonitrile solvent, k_2° values are found to

Table VI. Initial Velocities and Rate Coefficients for AgI Production in the Reaction of Neopentyl Iodide with $AgNO_3$–$AgClO_4$ Mixtures in Acetonitrile at 75.0°[a]

$[AgNO_3]$, M	$[AgClO_4]$, M	[Ionic strength], M	$10^7 V_i$, M sec^{-1}	$10^3 k_2$, M^{-1} sec^{-1}	$10^3(k_2 - \alpha k_2^\circ)$,[b] M^{-1} sec^{-1}
0.0448	0	0.0448	1.61	0.0850	0.0619
0.0361	0.0087	0.0448	1.47	0.0776	0.0545
0.0271	0.0178	0.0449	1.34	0.0710	0.0479
0.0179	0.0268	0.0447	1.18	0.0625	0.0394
0.0088	0.0359	0.0447	1.05	0.0555	0.0334
0	0.0446	0.0446	0.93	0.0491	0.0260

[a] [Neopentyl iodide] = 0.0422 M. [b] α = degree of dissociated $AgNO_3$ and $AgClO_4$ in CH_3CN; $\alpha k_2^\circ = (0.66)(0.035 \times 10^{-3}) = 0.0231 \times 10^{-3}$ M^{-1} sec^{-1}.

Table VII. The Ratio of Elimination (B) and the Distribution of Products for the Reaction of Neopentyl Iodide with $AgNO_3$, $AgClO_4$, and $AgNO_3$–Et_4NNO_3 Mixtures in Acetonitrile

[Salt], M	[Neop-I], M	Temp, °C	$[Et_4NNO_3]$, M	(100B), %	1-ene,[b] %	2-ene,[c] %
$[AgNO_3]$						
0.1999	0.1497	25.0		66.4	24.1	75.9
0.2010	0.2402	45.0		67.6		
0.1999	0.1497	45.0		72.5	34.2	65.8
0.1978	0.2218	45.0	0.0492	75.1[a]		
0.1005	0.2404	45.0		73.3		
0.1999	0.1497	75.0		70.2	39.3	60.7
0.0997	0.0984	75.0		68.2	40.8	59.2
$[AgClO_4]$						
0.2018	0.1709	25.0		100	16.5	83.5
0.2018	0.1709	45.0		92.3[a]	18.5	81.5
0.2018	0.1709	75.0		78.3[a]	17.6	82.4

[a] Initial B values as obtained by extrapolation. [b] 2-Methyl-1-butene expressed as percent of total alkene. [c] 2-Methyl-2-butene expressed as percent of total alkene.

vary only with the type of alkyl halide used, whereas the third-order constants for Y^--assisted reactions, $k_3^{Y^-}$, follow the order of nucleophilicity, $k_3^{NO_3^-} \gg k_3^{ClO_4^-}$.

Product Studies. Product formation in the reaction of neopentyl iodide with $AgNO_3$, $AgClO_4$, and $AgNO_3$–Et_4NNO_3 mixtures in acetonitrile has been studied at 25.0, 45.0, and 75.0°. The elimination reaction was followed by monitoring the rate of acid production, checked occasionally by the direct bromination method, while the overall rate was obtained from the rate of loss of Ag^+. The olefin proportion (B) was obtained for various percentages of the reaction from Figure 4. It has been observed that, both at 45.0 and 75.0°, the ratio B is rather insensitive to the initial concentration of $AgNO_3$ used (Table VII). However, the addition of Et_4NNO_3 causes a slight increase in the proportion of olefins produced. Thus, at 45.0°, the reaction in the absence of Et_4NNO_3 gave an average of 71% alkene, compared with 75% alkene with 0.049 M Et_4NNO_3 added.

In contradistinction to the $AgNO_3$ reaction, the one with $AgClO_4$ tends to yield generally more alkene (Table VI). Reaction at 25.0° yields solely olefins. However, for reactions carried out at 45.0 and 75.0°, the percentage olefin decreases to 92 and 78%, respectively. In this case, olefin formation appears to be favored at lower temperature while substitution and/or polymerization appears to have a higher activation energy.

Within the olefin proportion of the products formed in the attack of neopentyl iodide with $AgNO_3$ and $AgClO_4$, the distribution ratios of 2-methyl-1-butene and 2-methyl-2-butene have been quantitatively determined by gas–liquid chromatography (Table VII). For reactions with $AgNO_3$, increasing the reaction temperature caused the ratio of 2-methyl-1-butene to 2-methyl-2-butene to increase. However, the $AgClO_4$ reaction with neopentyl iodide gave approximately 17.5% 2-methyl-1-butene and 82.5% 2-methyl-2-butene, irrespective of the reaction temperature.

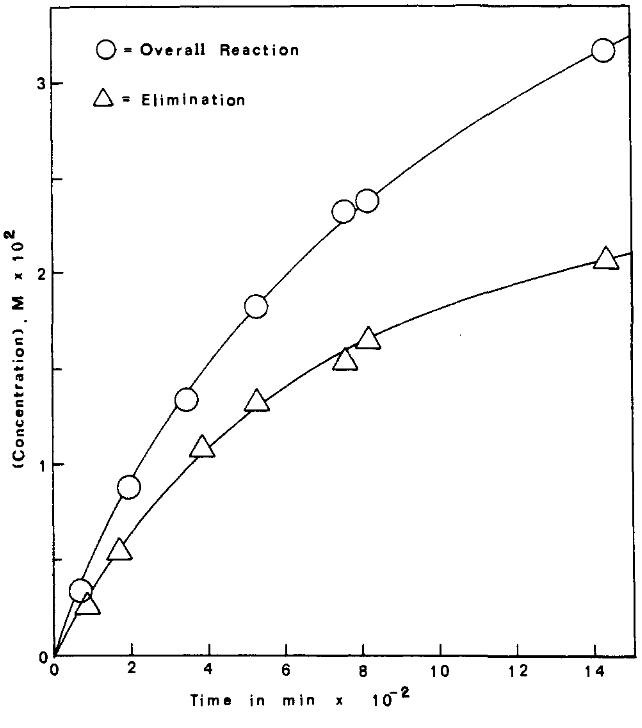
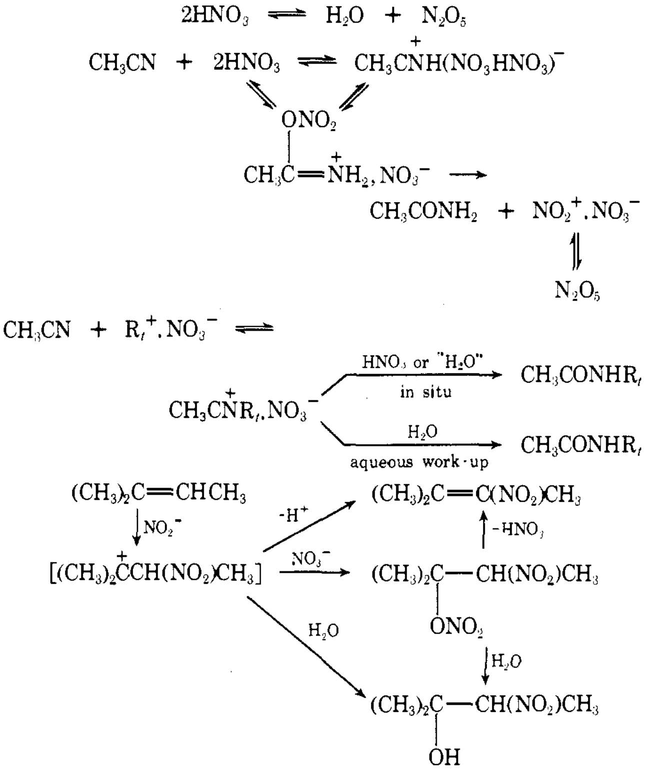


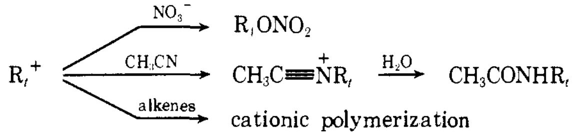
Figure 4. The rates of AgI production (○) and alkene formation (△) in the reaction of neopentyl iodide (0.0597 M) with $AgNO_3$ (0.0917 M) in CH_3CN at 75.0°.

A priori, it would appear that the reaction of neopentyl iodide with silver nitrate in acetonitrile proceeds, after rearrangement to the *tert*-amyl cation, with 70% elimination, and by inference, with 30% substitution. The detailed identification of all the initial substitution products is still in

Scheme II



progress: but, in principle, the *tert*-amyl cation (R_t^+) would be expected to yield the following "substitution" products:



In fact, the overall reaction is quite slow and, under the above conditions, *tert*-amyl nitrate undergoes, in acetonitrile, a unimolecular decomposition to give, inter alia, a mixture consisting of 2-methyl-2-butene, 2-methyl-1-butene, and nitric acid.[24] Starting with *tert*-amyl nitrate in acetonitrile, we find that acid development proceeds first to ca. 90% completion ($\tau_{1/2} \simeq 7 \times 10^3$ sec at 45°), when irreversible reactions set in, leading to the slow disappearance of nitric acid and of the two alkenes. Some possible subsequent side reactions are indicated in Scheme II.

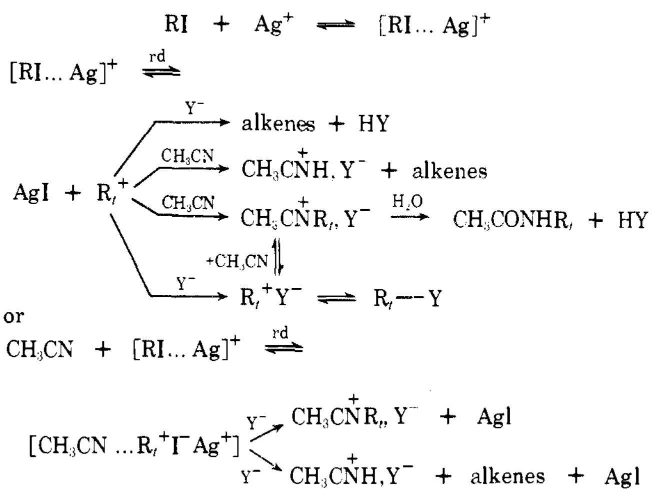
Discussion

In the absence of added tetraethylammonium salts, the reactions of neopentyl iodide with $AgNO_3$ and $AgClO_4$ in acetonitrile were found to exhibit the kinetic pattern given by eq 1. Furthermore, for reactions with added tetraethylammonium salts, the kinetics could also be satisfactorily analyzed, provided the concentration of free anion derived from the added salt is included, as shown in eq 3. Rate expressions 1 and 3 are actually identical if written in terms of free ions rather than in terms of stoichiometric concentrations (eq 7):

$$V_i = k_2^\circ[RI][Ag^+] + k_3^{Y^-}[RI][Ag^+][Y^-] \qquad (7)$$

Throughout this analysis, it is assumed that both silver and tetraethylammonium salts are incompletely dissociated in acetonitrile solvent and that their degrees of dissociation, α and α', respectively, are not significantly different.[22,23] The present work confirms an old suggestion by Euler and Olander[11] that, in the reaction of primary alkyl halides with silver salts, only free silver ions are capable of bringing to bear their full electrophilic capacity and thereby assist the heterolysis of the carbon halogen bond. Thus, in expressions 1 and 3, it was found necessary to incorporate the degree of dissociation of the salt, in order to convert the stoichiometric amount of the salt into the corresponding concentration of free ions.

Scheme III



Although detailed data for the activity coefficients of the silver and tetraethylammonium salts in acetonitrile are not available, it is possible to evaluate activity coefficients (γ) using the Debye-Hückel expression (eq 8) given by Coetzee[25] for acetonitrile ($D = 36$):

$$\log \gamma_i = -\frac{(1.64\,Z_i^2\,I^{1/2})}{(1 + 0.48aI^{1/2})} \qquad (8)$$

where I is the ionic strength, Z_i is the charge of the ith species, and a is the "distance of closest approach". For salt concentrations below 0.1 M, we have calculated γ values using a values ranging between 3.1 and 6.0 Å and, among these, the best fit was found for a = 6.0 Å, with γ values being almost identical with those of α, the degree of dissociation of the salts used.

The consistency of the results obtained with the general eq 7, for the reaction with and without tetraethylammonium salts, strongly supports a reaction proceeding via two concurrent pathways, one pseudo second order and the other third order. The first term, $k_2^\circ[RI][Ag^+]$, in eq 7 implies that only Ag^+ is effective as an electrophile and that the reaction occurs without assistance from the counterions; it probably involves a solvent molecule acting as a nucleophile in the rate-controlling step, $k_2^\circ = 0.035 \times 10^{-3}\ M^{-1}\ sec^{-1}$.

Thus, although it may be safe to assume that anionic assistance is absent from the first term in eq 7, it must not be overlooked that the solvent acetonitrile, being itself weakly nucleophilic, may participate in this step.[6c,17] A representation consistent with the term $k_2^\circ[RI][Ag^+]$ is shown in Scheme III.

As noted earlier, the first term, $k_2^\circ[RI][Ag^+]$, in eq 7 makes a significant contribution to the overall rate of reaction, particularly in dilute solutions and in the absence of moderate nucleophiles such as NO_3^-. However, in more concentrated solutions especially when the salt used possesses a nucleophilic counterion, the contribution from the third-order term, $k_3^{Y^-}[RI][Ag^+][Y^-]$, in eq 7 becomes prominent. Here the ionization of neopentyl iodide is concurrently being assisted both by the Ag^+ and its counterions, NO_3^- or ClO_4^-, in the rate-controlling step. The importance of anionic assistance is further underscored by the catalytic effect of added tetraethylammonium nitrate and/

Scheme IV

$$\mathrm{RI} + \mathrm{Ag}^+ \rightleftharpoons [\mathrm{RI}\ldots\mathrm{Ag}]^+$$

$$[\mathrm{RI}\ldots\mathrm{Ag}]^+ + \mathrm{Y}^- \overset{\mathrm{rd}}{\rightleftharpoons}$$

$$[\mathrm{Y}^-\mathrm{R}_t{}^+\mathrm{I}^-\mathrm{Ag}^+] \begin{array}{l} \nearrow \mathrm{R}_t\text{—}\mathrm{Y} + \mathrm{AgI} \\ \searrow \text{alkenes} + \mathrm{HY} + \mathrm{AgI} \end{array}$$

or perchlorate (Tables IV and V). Anionic assistance is further documented in studies using mixed $AgNO_3$–$AgClO_4$ solutions (Figure 3). All these lines of evidence indicate that the anion participates in the rate-determining step of these Ag^+-catalyzed reactions by assisting the ionization of the alkyl halide.[2-6] For neopentyl iodide reactions at 75.0° we calculate the ratio $k_3^{NO_3^-}/k_3^{ClO_4^-}$ to be 2.44. This is in the order of nucleophilicity of the anions, $NO_3^- > ClO_4^-$, although the magnitude is much reduced from their relative S$_\mathrm{N}$2 reactivity.[26]

A mechanistic scheme consistent with the term $k_3^{Y^-}\cdot[Ag^+][RI][Y^-]$ which emphasizes anionic participation in the rate-determining step is shown in Scheme IV.

The values of $k_3^{NO_3^-}$ and $k_3^{ClO_4^-}$ remain constant up to 0.065 *M* silver salt. Deviations in the third-order rate constants become apparent when the concentration of the silver salt exceeds 0.07 *M* (Tables I and II). Both silver and tetraethylammonium salts in acetonitrile have been shown by Raman[22] and conductance[23] studies to be incompletely dissociated. At infinite dilution, the degree of dissociation of these salts approaches unity ($\alpha \rightarrow 1$) but, at high salt concentration, a significant proportion is present as ion pairs. Below 0.07 *M* silver salt, the respective ion pairs do not appear to be sufficiently numerous nor sufficiently effective as electrophiles with respect to neopentyl iodide to contribute significantly to the overall rate. However, in more concentrated solutions, these ion pairs are both more numerous and less well solvated[22,23] and would be expected to contribute significantly to the overall rate. In this case then, the rate form seems to contain contributions from higher order terms; such contributions may serve to explain the apparent increase in $k_3^{Y^-}$ values at higher salt concentrations.

In all instances, direct substitution products could not be isolated despite exhaustive attempts and the reaction of neopentyl iodide with silver salts always yielded elimination and substitution products, which are derived from the *tert*-amyl cation.[15,19,27] The attack on neopentyl iodide by $AgNO_3$ and $AgClO_4$ gave a mixture of 2-methyl-1-butene and 2-methyl-2-butene. The distribution of the two alkenes has been found to be consistent with that obtained in the unimolecular reactions involving encumbered cations produced by solvolysis.[28] These reactions favor elimination to the more substituted and certainly the more stable olefin. For $AgNO_3$ reactions, a temperature increase tends to yield increasing amounts of 2-methyl-1-butene. In contrast, the relative amounts of the two olefins formed in the $AgClO_4$ reactions seemed to be unaffected by temperature. The $AgClO_4$ reaction shows quite a different proportion of elimination to substitution products from that of the corresponding $AgNO_3$ reaction. For a given temperature, a greater degree of elimination was noted in the case of attack by $AgClO_4$ (100% at 25.0°), but accompanying side reactions seemed to be favored by a rise in temperature. These differences can in part be justified by examining the nucleophilicity of NO_3^- vs. ClO_4^- and the relative stability of the initial substitution products, *tert*-amyl nitrate and *tert*-amyl perchlorate. *tert*-Amyl perchlorate in contrast to *tert*-amyl nitrate is known to be exceptionally labile and in acetonitrile solution can be considered as a good source of carbonium ions, which can either lose a proton to give a mixture of 2-methyl-1-butene and 2-methyl-2-butene or alternatively, by analogy with known reactions of several easily ionizable alkyl esters, react with acetonitrile solvent to produce, upon hydrolysis, the *N*-(*tert*-amyl)acetamide.[3,6d,17]

Experimental Section

Materials. Acetonitrile (Baker Analyzed Reagent Grade) was dried by adding triphenylmethyl fluoroborate[29] until a yellow solution persisted, and the acetonitrile was then distilled from an all-glass system through a 2-ft jacketed column packed with glass helices. The constant boiling fraction, bp 80–81°, was collected and stored under N_2 in an air-tight bottle: $n^{21.5}\mathrm{D}$ 1.3449 (lit. $n^{20}\mathrm{D}$ 1.3441).

Silver nitrate (Allied Chemical Reagent Grade) was dried in an oven at 120° for 3 hr and used without further purification.

Silver perchlorate (The G. Frederick Smith Chemical Co.) was dried at 120° for several hours and cooled. Dry benzene was then saturated with the anhydrous $AgClO_4$, and the solution was carefully distilled to remove traces of water. The solution was cooled to room temperature and then treated with dry pentane. The precipitated $AgClO_4$ was collected by rapid suction filtration in a dry bag in the dark, and the white powdery mass was immediately vacuum dried to a constant weight to give an analytically pure product.

Tetraethylammonium nitrate was prepared from a 10% aqueous solution of tetraethylammonium hydroxide (Eastman) by neutralizing slowly with concentrated Analar grade nitric acid (Allied Chemical) until the pH of the solution was about 6. The solution was evaporated to dryness under reduced pressure and the solid recrystallized from mixed acetonitrile–ether solvent and dried under vacuum.

Tetraethylammonium perchlorate (Eastman) was dried under vacuum and used without further purification.

Neopentyl iodide was prepared from neopentyl alcohol (Aldrich Chemical) according to the method of Landauer and Rydon.[30] The crude product was purified by the procedure of Kornblum and Iffland[31] followed by a final distillation through a Vigreux column. The constant boiling fraction, bp 68.0° (88 mmHg) [lit. 71° (100 mmHg)],[31] was collected and stored under N_2. $n^{21.5}\mathrm{D}$ 1.4897 (lit. $n^{20}\mathrm{D}$ 1.4888). The purity of the neopentyl iodide prepared was further assayed using gas–liquid chromatography, HP Model 5750, column: ⅛ in. × 20 ft, 5% GP 39 (di-*n*-decylphthalate on Anakrom ABS 100–110 mesh). Impurities found were 2-methyl-1-butene and 2-methyl-2-butene in an overall amount averaging 0.5% as determined by direct bromination.

Kinetic Measurements. All solutions used were made up and standardized (for silver salts) at 25.0° unless otherwise stated. The concentrations quoted throughout were measured at room temperature and were uncorrected for solvent expansion at elevated temperatures. All potentiometric titrations were done on a Radiometer automatic titrator (Model TTT1c) equipped with auto-burette unit ABU1b, Radiometer Type SBR2c titrigraphic recorder, and scale expander PHA 630T. Specifically for silver ion or halide ion titrations the silver (P401)–mercurous sulfate (K601) electrodes were used. All the kinetic runs conducted at 75° were carried out using the sealed bulb technique. The sealed tubes were derived from 16 × 150 mm Pyrex test tubes which were constricted and filled via automatic pipets of equal volume (5.00 ml) with both alkyl halide and silver salt solutions, stoppered, the contents frozen in Dry Ice–acetone slush and then sealed. After rapid thawing under a continuous flow of warm water, the tubes were then shaken vigorously and all were immersed simultaneously into a constant water temperature bath. Three minutes was the usual time for the reaction mixture to attain thermal equilibrium after which the tubes were removed at regular intervals and stored in Dry Ice–acetone bath until opened and analyzed by potentiometric titration: (a) kinetic runs in the absence of silver salts were followed by potentiometric titration with standard aqueous $AgNO_3$ solution; (b) kinetic runs in the presence of silver salts were monitored by the rate of loss of Ag^+, the samples were potentiometrically titrated against standard NaCl solution.

Product Studies. All product studies were done on the kinetic run scale having to remove aliquots at regular intervals for the following measurements.

(A) Extent of Acid Formation. Reaction samples were obtained at regular intervals according to the procedure described under Kinetic Measurements. The frozen samples were then thawed, and the excess Ag^+ was rapidly removed by quenching with 30 ml of LiCl in saturated dry acetone, previously rendered neutral to lacmoid indicator. The solution was cooled in Dry Ice–acetone slush and titrated against a standard solution of sodium methoxide using lacmoid indicator.

(B) Extent of Olefin Formation by the Direct Bromination Method. The contents of the tubes were thawed and washed out with distilled water into 20 ml of glacial acetic acid (Baker Analyzed Reagent Grade). A standard solution of bromine in glacial acetic acid was then added to the reaction mixture in excess of the amount required to brominate any olefins present and then, after several seconds of swirling, an excess of KI (Mallinckrodt Analytical Reagent Grade) was added followed by distilled water to make up to 50 ml volume. The iodide liberated was titrated against standard $Na_2S_2O_3$ using starch as an indicator. Concurrently, blank experiments were run in order to ensure an accurate end point.

(C) Distribution of 2-Methyl-1-butene and 2-Methyl-2-butene. Analytical gas–liquid chromatography was carried out using a Hewlett-Packard Research Gas Chromatograph Model 5751B, equipped with two flame ionization detectors and disc integrator–recorder. The column used was a ⅛ in. × 20 ft stainless steel packed with 5% GP39 di-*n*-decylphthalate on Anakrom ABS 100–110 mesh. At the injection port, 3 in. of the column was packed with glass wool to hold back the silver salts since the reaction mixtures were injected directly without isolation.

Control Run. Equal concentrations of 2-methyl-1-butene and 2-methyl-2-butene were made up in acetonitrile solvent, and then 1-μl samples were injected into the GLC. The gas chromatograph was operated under the following conditions. Temperature programming was used, set with 3 min post injection time at 25°, and then the temperature was increased to 100° at a rate of 6°/min. Pre-purified N_2 was used as the carrier gas whose flow rate was 30 ml/min. The retention times obtained were found to be 150 and 180 sec for 2-methyl-1-butene and 2-methyl-2-butene, respectively. The peaks were symmetrical, and their areas corresponded to the relative amount of the two alkenes. To check for sensitivity, the presence of more than 1.0% of either alkene could be detected by calibrating the instrument with a mixture of the two alkenes in acetonitrile in the ratio of 100:1 and analyzing it under similar conditions.

Actual Run. Thawed samples were kept cold at 0° in a vial, and each time 1-μl samples were injected directly into the gas chromatograph. At least two injections were made to check for reproducibility (±1.0%). The relative areas under the peaks represent the amounts of alkenes formed in the reaction. For every run, the distribution of 2-methyl-1-butene and 2-methyl-2-butene have to be corrected for the initial presence of the alkenes, where the kinetic zero corresponds to 3 min immersion in temperature bath.

References and Notes

(1) (a) Previous paper in this series: Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 5060 (1965). (b) Supported in part by U.S. Public Health Service Grants. (c) For further details, cf. W.-H. Wong, Ph.D. Dissertation in Chemistry, University of Washington, 1971; W.-H.W. was a Petroleum Research Fund–American Chemical Society Fellow, 1969–1970. (d) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) G. S. Hammond, M. F. Hawthorne, J. W. Waters, and B. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960).

(3) Y. Pocker and D. N. Kevill, *J. Am. Chem. Soc.*, **87**, 4760, 4771, 4775 (1965).

(4) F. G. Donnan and K. A. Burke, *Z. Phys. Chem.* (*Leipzig*), **69**, 148 (1909); G. Senter, *J. Chem. Soc.*, **97**, 346 (1910); **99**, 95 (1911); J. N. Pearce and A. M. Weigle, *Amer. Chem. J.*, **48**, 243 (1912); M. Murakami, S. Dac, and S. Takeuchi, *Bull. Chim. Soc. Jpn.*, **24**, 1 (1957); E. Melendez and C. Prevost, *Bull. Soc. Chim. Fr.*, 1232 (1964); *ibid.*, 2103 (1965); P. S. Walton and M. Spiro, *J. Chem. Soc. B*, 42 (1969); J. M. Austin, O. D. E. S. Ibrahim, and M. Spiro, *ibid.*, 669 (1969); E. S. Rudakov, V. D. Belyaev, and V. V. Zamaschikov, *Reakts. Sposobn. Org. Soedin.*, **8**, 207 (1971); P. Beak and J. A. Barron, *J. Org. Chem.*, **38**, 2771 (1973); D. N. Kevill and L. Held, *ibid.*, **38**, 445 (1973); O. A. Reutov, A. S. Gudkova, G. P. Brusova, T. P. Reutov, and E. I. Troyanski, *Zh. Org. Khim.*, **9**, 1801 (1973).

(5) (a) D. W. Colcleugh and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 2542 (1964); (b) D. N. Kevill and V. V. Likhite, *Chem. Commun.*, 247 (1967); D. N. Kevill, G. H. Johnson, and V. V. Likhite, *Chem. Ind.* (*London*), 1555 (1969); E. S. Rudakov, V. V. Zamashchikov, and V. D. Belyaev, *Reakts. Sposobn. Org. Soedin.*, **9**, 31 (1974).

(6) (a) N. Kornblum, W. J. Jones, and D. E. Hardies, *J. Am. Chem. Soc.*, **88**, 1704 (1966); (b) N. Kornblum and D. E. Hardies, *ibid.*, **88**, 1707 (1966); (c) R. A. Bartsch and G. M. Pruss, *J. Org. Chem.*, **37**, 458 (1972).

(7) T. Cohen and J. Solash, *Tetrahedron Lett.*, **27**, 2513 (1973).

(8) K. A. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

(9) I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 169 (1946).

(10) F. G. Donnan and H. E. Potts, *J. Chem. Soc.*, **97**, 1882 (1910).

(11) H. V. Euler and A. Olander, *Z. Elektrochem.*, **36**, 506 (1930).

(12) M. F. Redies and T. Iredale, *J. Phys. Chem.*, **48**, 224 (1944).

(13) See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1969, pp 479–483; cf. also, E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 1236 (1937).

(14) J. A. Vona and J. Steigman, *J. Am. Chem. Soc.*, **81**, 1095 (1959).

(15) M. L. Bender and H. Robbins, *J. Am. Chem. Soc.*, **78**, 1699 (1956).

(16) C. Prevost and E. Singer, *Bull Soc. Chim. Fr.*, 1068 (1950); C. Prevost and R. Boyer, *ibid.*, 782 (1949).

(17) J. J. Ritter and P. Minieir, *J. Am. Chem. Soc.*, **70**, 4045 (1948); H. Plaut and J. J. Ritter, *ibid.*, **73**, 4076 (1951); J. Cast and T. S. Stevens, *J. Chem. Soc.*, 4180 (1953); S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954); G. W. H. Cheeseman, *Chem. Ind.* (*London*), 281 (1954); G. S. Hammond, W. D. Emmons, C. O. Parker, B. M. Graybill, J. H. Waters, and M. F. Hawthorne, *Tetrahedron, Suppl. 1*, **19**, 177 (1963).

(18) S. Winstein and R. E. Buckle, *J. Am. Chem. Soc.*, **64**, 2780 (1942).

(19) P. S. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **64**, 2633 (1942).

(20) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. Legall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).

(21) J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966).

(22) K. Balasubrahmanyam and G. J. Janz, *J. Am. Chem. Soc.*, **92**, 4189 (1970).

(23) I. M. Kolthoff and F. G. Thomas, *J. Phys. Chem.*, **69**, 3049 (1965); G. J. Janz, A. E. Marcinkowsky, and I. Ahmad, *J. Electrochem. Soc.*, **112**, 104 (1965).

(24) A referee has kindly drawn our attention to a paper by D. N. Kevill and R. F. Suthoff, *J. Chem. Soc. B*, 366 (1969), describing the kinetics of the relatively facile decomposition of *tert*-butyl nitrate in acetonitrile.

(25) J. F. Coetzee, *Prog. Phys. Org. Chem.*, **4**, 45 (1967).

(26) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953); Samuel P. McManus, "Organic Reactive Intermediates", Academic Press, New York, N.Y., 1973, p 300.

(27) F. C. Whitmore, E. L. Wittle, and A. H. Popkin, *J. Am. Chem. Soc.*, **61**, 1586 (1939); I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 166 (1946); P. S. Skell, I. Starer, and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960); G. J. Karabatsos and J. D. Graham, *Ibid.*, **82**, 5250 (1960); G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **86**, 1994 (1964).

(28) J. T. Keating and P. S. Skell, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 593.

(29) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(30) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

(31) N. Kornblum and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6653 (1955).