Electrophilic Catalysis in Nucleophilic Substitution and Elimination. VIII. Kinetics and Mechanism of Reaction of *tert*-Amyl and 1-Adamantylcarbinyl Halides with Silver Salts 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*

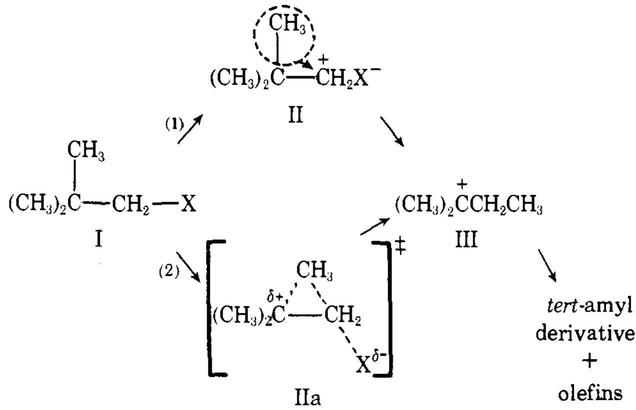
Abstract: The kinetics of reactions of *tert*-amyl chloride with $AgNO_3$, and 1-adamantylcarbinyl iodide with $AgNO_3$, $AgClO_4$, and AgTFA have been investigated in detail in acetonitrile. The reaction rates were followed by monitoring the rate of loss of Ag^+ and the kinetic results are found to conform to the expression, $V_i = k_2{}^{\circ}[RX][Ag^+] + k_3{}^{Y^-}[RX][Ag^+][Y^-]$. Anionic participation associated with the $k_3{}^{Y^-}$ term is further documented in experiments with added Et_4NNO_3. Also, the relative rates 6.7:2.6:1.0 for $k_3{}^{TFA^-}$: $k_3{}^{NO_3^-}$:$k_3{}^{ClO_4^-}$ in the reactions of 1-adamantylcarbinyl iodide with the respective silver salts follow the order of nucleophilicity of the anions $CF_3CO_2^- > NO_3^- > ClO_4^-$, although much reduced from their relative SN2 reactivity. The kinetic results of neopentyl and 1-adamantylcarbinyl iodide reactions are considered in relation to both structure and ease of rearrangement. The relative rates of 1-adamantylcarbinyl iodide to neopentyl iodide are 2.1:1.0 and 2.0:1.0 for reactions with $AgNO_3$ and $AgClO_4$, respectively. The results taken along with those obtained from product studies on neopentyl and *tert*-amyl halides allow a more detailed characterization of the ionization process. Evidence is presented in favor of a stepwise ionization-rearrangement mechanism in the neopentyl system.

The reactions of neopentyl iodide with $AgNO_3$ and $AgClO_4$ with and without added neutral tetraethylammonium perchlorate and nitrate have been investigated in some detail.[1a] Neopentyl iodide with its steric bulk tends to always resist any direct SN2 reactions. Nevertheless we have provided concrete evidence that the counterion participates in the rate-determining step of the Ag^+-assisted ionization of the C–I bond.[1a] Anions NO_3^- and ClO_4^- both caused rate enhancements, the former more than the latter; but with the latter, nucleophilic solvent intervention effectively competes with ClO_4^- participation.[1a,2,3] In all instances, the reaction is consistent with the kinetic scheme shown in eq 1.

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

It is well known that, in the reactions of neopentyl compounds under SN1 conditions, the isolated products are derived from the *tert*-amyl cation intermediate ($R_t{}^+$).[4] Product and kinetic studies of the reaction of neopentyl iodide with silver salts in acetonitrile had led us to propose a rate-determining formation of the quadruplet $Y^-R_t{}^+X^-Ag^+$.[1a] Consequently we considered it necessary to find out if anionic assistance also occurs in the corresponding reactions of *tert*-amyl halides. In addition, we found it advantageous to compare the products derived from the reactions of neopentyl and *tert*-amyl halides with silver salts in our attempt to characterize the type of intermediates present in these reactions.

Skeletal rearrangements involving the classic neopentyl derivatives have long been known and extensively studied. Despite these concentrated efforts, controversies still surround the various mechanisms involved in neopentyl rearrangement reactions. In the neopentyl system, in almost all cases, methyl migration has been confirmed, and most of the present day studies have been directed toward answering a question posed by Skell and Hauser in 1942.[5] If a neopentyl derivative ($(CH_3)_3CCH_2X$) is permitted to ionize where X^- is the departing group, is the methyl migration occurring (1) in a stepwise manner, after formation of the neopentyl cation (or ion pair) which exists as a discrete intermediate or (2) concurrently with ionization?



Most of the research on the mechanism of the neopentyl rearrangement has been concerned with finding evidence for or against the above proposed pathways.[6,7] The evidence available is best classified into three categories: (a) evidence for a concerted ionization and rearrangement;[5,8] (b) evidence for stepwise ionization and rearrangement;[7,9] and (c) evidence for the methyl-bridged carbonium ion intermediate.[10] Thus, in testing the generality of the kinetics and mechanism of silver salt catalysis, it proved both desirable and advantageous to have a neopentyl-type system which would react by an ionic mechanism and still not rearrange. Such a system would make it possible to exclude methyl participation as the driving force in Ag^+ catalysis and would allow a direct comparison of the reaction rate with that of the corresponding neopentyl derivative. Because of the great driving force for conversion of a primary to a tertiary carbonium ion, it might at first seem difficult to find a neopentyl system that does not rearrange under SN1-type conditions. 1-Adamantylcarbinyl systems possess a neopentyl structure but have considerable steric bias against rearrangement, and Nordlander et al. have considered their solvolyses in comparison with those of neopentyl derivatives.[7] By analogy, we have studied the kinetics of reaction of 1-adamantylcarbinyl iodide with silver salts, in the hope of delineating the mechanisms operative in silver ion assisted reactions.

Table I. Initial Velocities and Rate Coefficients for the Reaction of *tert*-Amyl Chloride with $AgNO_3$ in CH_3CN at 25.0°

$[AgNO_3]$, M	$[RCl]$, M	α^a	$10^7 V_i$, $M\ sec^{-1}$	$10^3 k_2$,^{b} $M^{-1}\ sec^{-1}$	$10^3 (k_2 - \alpha k_2°)$,^{c} $M^{-1}\ sec^{-1}$	$10^3 k_3^{NO_3^-}$,^{d} $M^{-2}\ sec^{-1}$
0.0030	0.0500	0.93	0.260	0.173	0.028	10.8
0.0060	0.0500	0.90	0.573	0.191	0.051	10.5
0.0124	0.0500	0.790	1.27	0.204	0.081	10.5
0.0250	0.0499	0.720	3.22	0.258	0.136	10.5
0.0503	0.0479	0.650	8.30	0.346	0.245	11.6

$^a\alpha$ = degree of dissociation of $AgNO_3$ (ref 11). $^b V_i = k_2[RCl][AgNO_3]_S$. $^c k_2° = 0.156 \times 10^{-3} M^{-1} sec^{-1}$. $^d k_3^{NO_3^-} = (k_2 - \alpha k_2°)/(\alpha^2[AgNO_3]_S)$.

Table II. Second-Order Rate Constants (k_2) for the Reaction of *tert*-Amyl Chloride with $AgNO_3$ in CH_3CN at 25.0°^{a}

Time, sec	$[AgCl]$, M	$10^3 k_2$, $M^{-1}\ sec^{-1}$
5700	0.0017	0.252
12000	0.0036	0.270
20400	0.0055	0.259
48000	0.0105	0.258
64200	0.0125	0.253
75720	0.0136	0.248
89220	0.0151	0.255

^{a} [*tert*-Amyl chloride] = 0.050 M; $[AgNO_3]_S$ = 0.025 M.

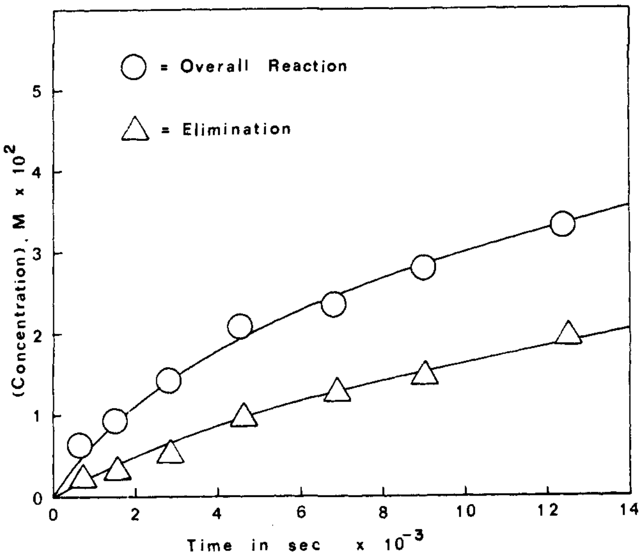


Figure 1. The rates of AgCl production (○) and alkene formation (△) in the reaction of *tert*-amyl chloride (0.1222 M) with $AgNO_3$ (0.0815 M) in CH_3CN at 25.0°.

Results

A. Reactions of *tert*-Amyl Halides. The reaction of *tert*-amyl chloride and silver nitrate has been briefly investigated in acetonitrile at 25.0°. The second-order rate coefficients extrapolate at infinite dilution to a finite value, $k_2° = 0.156 \times 10^{-3} M^{-1} sec^{-1}$. The kinetics of the overall reaction (Table I) are well represented by the expression in eq 2.

$$V_i = \alpha k_2°[RCl][AgNO_3]_s + \alpha^2 k_3^{NO_3^-}[RCl][AgNO_3]_s^2 \quad (2)$$

The mean value of $k_3^{NO_3^-}$ is $10.9 \times 10^{-3} M^{-2} sec^{-1}$, indicating that the *tert*-amyl chloride reaction with $AgNO_3$ follows the same kinetic pattern as that described in the previous paper.[1a]

Furthermore, the constancy of the second-order rate coefficients throughout any given run (Table II) shows that there is little or no autocatalysis by the precipitated AgCl.[3] The ratios of elimination to overall reaction (B) for the reactions of *tert*-amyl chloride and iodide with silver nitrate and perchlorate in the presence and absence of tetraethylammonium nitrate are given in Table III. The proportion of the reaction undergoing elimination is determined by monitoring the rate of nitric or perchloric acid production, while the overall rate of reaction is measured by rate of loss of Ag^+ from solution (Figure 1). The ratio of elimination to overall reaction at a given temperature is found to be essentially the same (B = 0.41, Table III). In addition, it can also be inferred that irrespective of the leaving group, either iodide or chloride, the B ratios are 0.41 and 0.47₅ at 25.0 and 45.0°, respectively.

The distribution ratios of 2-methyl-1-butene and 2-methyl-2-butene reported in Table III show that the more stable internal olefin predominates ([2-ene]:[1-ene] = 2.3 at 25.0°) and that an increase in the reaction temperature favors the formation of terminal alkene ([2-ene]:[1-ene] = 2.0 at 45.0°). With $AgClO_4$ at a given temperature, the olefins 2-methyl-1-butene and 2-methyl-2-butene are formed in a different ratio ([2-ene]:[1-ene] = 5.0 at 25.0°) which is nevertheless insensitive as to whether *tert*-amyl chloride or iodide is used.

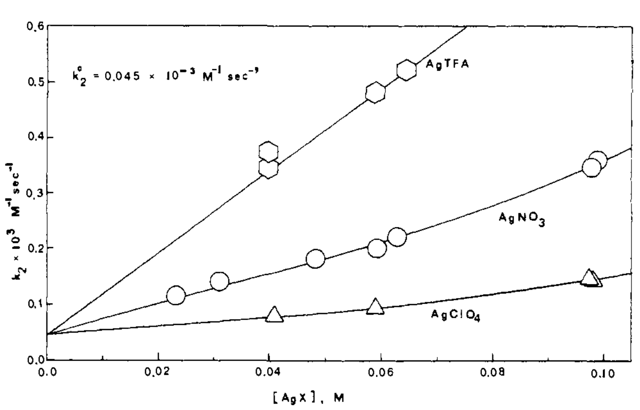


Figure 2. Dependence of the observed second-order rate coefficients, k_2, on silver salt concentration for the reaction of 1-adamantylcarbinyl iodide with AgTFA (⬡), $AgNO_3$ (○), and $AgClO_4$ (△) in CH_3CN at 75.0°.

B. Reactions of 1-Adamantylcarbinyl Iodide. 1-Adamantylcarbinyl iodide, with its considerable bias against S_N2, is found to react very slowly with tetraethylammonium nitrate. An acetonitrile solution containing 0.0850 M 1-adamantylcarbinyl iodide and 0.200 M Et_4NNO_3 reacted at 75.0° to the extent of only 1.6% in the iodide after 6 days. Clearly, any direct substitution reaction on the alkyl halide must be negligible in comparison with the rate of electrophilic catalysis by silver salts. In contrast, the reactions of 1-adamantylcarbinyl iodide with silver trifluoroacetate, nitrate, and even perchlorate proceed readily in acetonitrile at 75.0°, and the second-order rate coefficients (k_2) for all these reactions have been determined (Table IV). Plots of k_2 vs. silver salt concentration yield a family of lines which on extrapolation to infinite dilution intersect the k_2 axis at an identical point, $k_2° = 0.045 \times 10^{-3} M^{-1} sec^{-1}$ (Figure 2). In general, the initial rates (V_i) follow the kinetic expression represented by eq 1.

Table III. The Ratio of Elimination to Overall Reaction (B) and the Product Distribution for the Reaction of *tert*-Amyl Chloride and Iodide with $AgNO_3$, $AgClO_4$, and $AgNO_3$–Et_4NNO_3 Mixtures in Acetonitrile

Temp, °C	[*tert*-Amyl-Cl], M	[*tert*-Amyl-I], M	[$AgNO_3$], M	[$AgClO_4$], M	[Et_4NNO_3], M	100 B, %	1-ene,[b] %	2-ene,[c] %
25	0.1222		0.0815			41.0[a]		
25	0.1222		0.0935			42.2[a]		
25	0.0538		0.2010			40.9		
25	0.0538		0.2010		0.0492	43.5		
25	0.1433		0.2090			40.0		
45	0.0538		0.201			47.4		
25		0.1082	0.2007			40.6	29.6	70.4
45		0.1082	0.2007			47.5	33.0	67.0
25	0.1260			0.2009		84.3	16.7	83.3
75	0.1260			0.2009		61.0	16.3	83.7
25		0.1082		0.2023		80.5	15.2	84.8
45		0.1082		0.2023		73.2	14.0	86.0

[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.

Table IV. The Reaction of 1-Adamantylcarbinyl Iodide with $AgNO_3$, $AgClO_4$, and AgTFA in Acetonitrile at 75.0°

[$AgNO_3$], M	[$AgClO_4$], M	[AgTFA],[a] M	[Adm-I], M	[Et_4NNO_3], M	α[b]	α'	$10^7 V_i$, M sec^{-1}	$10^3 k_2$,[c] M^{-1} sec^{-1}	$10^3 k$,[d] M^{-1} sec^{-1}	$10^3 k_3{}^{Y^-}$, M^{-2} sec^{-1}
0.0233			0.0418		0.720		1.10	0.133	0.081	6.69
0.0310			0.0248		0.710		1.07	0.139	0.107	6.85
0.0484			0.0421		0.650		3.69	0.181	0.152	7.44
0.0595			0.0492		0.635		5.95	0.203	0.174	7.28
0.0629			0.0241		0.630		3.35	0.221	0.193	7.71
0.0981			0.0196		0.570		6.66	0.346	0.320	10.10
0.0986			0.0415		0.570		14.60	0.356	0.330	10.30
0.0310			0.0248	0.0276	0.590	0.710	1.48	0.193	0.166	7.45
0.0310			0.0248	0.0797	0.470	0.580	1.74	0.226	0.205	7.00
0.0310			0.0248	0.1208	0.410	0.540	1.92	0.250	0.232	7.35
	0.0409		0.0421		0.680		1.39	0.081	0.050	2.67
	0.0588		0.0490		0.620		2.68	0.093	0.065	2.88
	0.0970		0.0244		0.570		3.49	0.146	0.120	3.88
	0.0925		0.0415		0.570		5.96	0.147	0.121	3.84
		0.0403	0.0120		0.680		1.82	0.377	0.346	18.60
		0.0402	0.0245		0.680		3.38	0.342	0.311	16.70
		0.0588	0.0491		0.620		13.90	0.480	0.452	19.70
		0.0645	0.0245		0.620		8.21	0.520	0.492	19.90

[a] AgTFA = Silver trifluoroacetate. [b] α = degree of dissociation in CH_3CN.[11] [c] Observed second-order rate coefficients. [d] $k = (k_2 - \alpha k_2{}^\circ)$ where $k_2{}^\circ = 0.045 \times 10^{-3} M^{-1}$ sec^{-1}.

At a particular temperature and substrate concentration, the first term in eq 1 is a function only of the concentration of dissociated Ag^+, irrespective of the type of silver salt used. Each third-order term describes the concurrent intervention by the electrophilic Ag^+ as well as the nucleophilic counterion Y^-. Below 0.07 M silver salt, the coefficients, $k_3{}^{TFA^-}$, $k_3{}^{NO_3^-}$, and $k_3{}^{ClO_4^-}$ appear to be essentially constant. The mean values of the third-order rate constants $k_3{}^{TFA^-}$, $k_3{}^{NO_3^-}$, and $k_3{}^{ClO_4^-}$ are 18.7×10^{-3}, 7.19×10^{-3}, and 2.77×10^{-3} M^{-2} sec^{-1}, respectively. For silver salt concentration above 0.07 M, the third-order rate constants increase gradually possibly because of the incursion of ion-pair catalysis.[3]

In studies with added tetraethylammonium nitrate, the specific participation by NO_3^- was scrutinized (Figure 3), and the results obtained strongly suggest anionic assistance in the rate-determining step. The initial rate is found to be consistent with eq 3

$$V_i = \alpha k_2{}^\circ[RI][AgNO_3]_s + \alpha k_3{}^{NO_3^-}[RI] \times [AgNO_3]_s(\alpha[AgNO_3]_s + \alpha'[Et_4NNO_3]_s) \quad (3)$$

and the $k_3{}^{NO_3^-}$ rate constants thus obtained have a mean value of 7.16×10^{-3} M^{-2} sec^{-1}, which is practically identical with the one obtained in the absence of added Et_4NNO_3, $k_3{}^{NO_3^-} = 7.19 \times 10^{-3}$ M^{-2} sec^{-1} (Table IV).

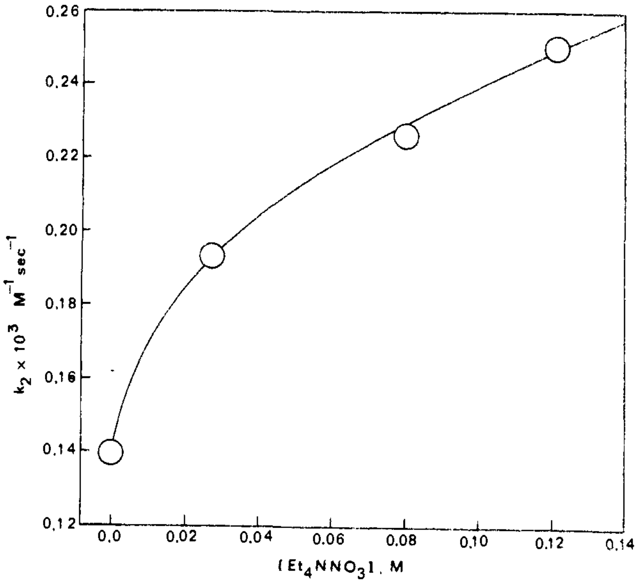


Figure 3. Dependence of the second-order rate coefficients, k_2, on the concentration of Et_4NNO_3 in the reaction of 1-adamantylcarbinyl iodide with $AgNO_3$ in CH_3CN at 75.0°.

Discussion

Our investigations of silver salt catalysis have been mainly directed toward understanding the role of the anion in the rate-controlling step and also toward delineating the mechanisms of these complex reactions.

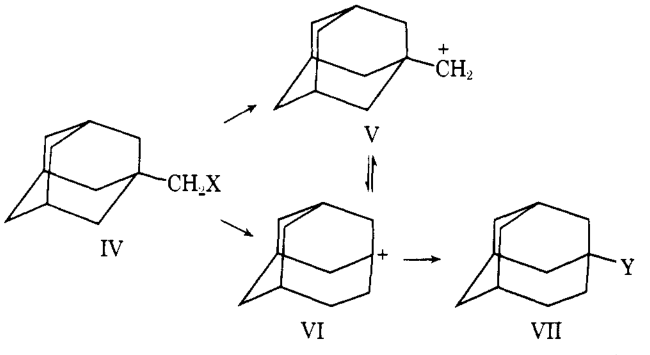
Table V. Second-Order Rate Constants Associated with Ag^+ Catalysis, in M^{-1} sec^{-1}, for Various Alkyl Halides in CH_3CN

Alkyl halide	Temp, °C	$10^3 k_2°$, M^{-1} sec^{-1} AgNO$_3$	AgClO$_4$	AgTFA
Neopentyl iodide[a]	75.0	0.035	0.035	
1-Adamantylcarbinyl iodide	75.0	0.045	0.045	0.045
tert-Amyl chloride	25.0	0.156	0.156	

[a] Values taken from ref 1a.

The kinetic results for the reactions of *tert*-amyl chloride and 1-adamantylcarbinyl iodide with silver nitrate, perchlorate, and trifluoroacetate suggest that the kinetic form originally proposed for the reactions neopentyl iodide with silver salts is obeyed (eq 1).[1a] *tert*-Amyl chloride is a compound that ionizes readily even under mild conditions to give directly the stable *tert*-amyl cation; neopentyl iodide is a primary compound, well-known for its rearrangement when subjected to conditions which favor SN1-type mechanisms; whereas 1-adamantycarbinyl iodide, while possessing the steric bulk of the neopentyl system, lacks its ability to rearrange.[7] Because of their structural differences, the $k_2°$ values which measure the rate of ionization catalyzed by Ag^+ with possible assistance from CH_3CN, but without assistance from the counterions, are found to be different for the various substrates (Table V). Perhaps the most striking result is that, under these limiting conditions, 1-adamantylcarbinyl iodide is actually 1.29 times more reactive than neopentyl iodide.

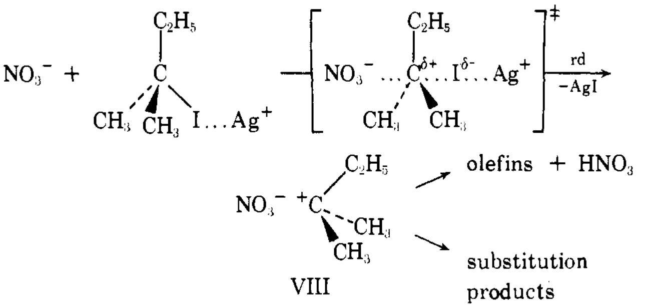
Despite the differences in structural properties, anionic assistance has been documented with all three halides. From the reaction of neopentyl and 1-adamantylcarbinyl iodides with silver salts at 75.0°, the ratios, $k_3^{NO_3^-}/k_3^{ClO_4^-}$, are found to be 2.44 and 2.60, respectively. The relative ratios for the reaction of 1-adamantylcarbinyl iodide with the three silver salts used are 6.75:2.60:1.00 for $k_3^{TFA^-}:k_3^{NO_3^-}:k_3^{ClO_4^-}$. This is the order of nucleophilicity of these anions, $CF_3CO_2^- > NO_3^- > ClO_4^-$, although much reduced from their relative SN2 reactivity. This strongly supports the contention that the anion participates in the rate-determining step of these reactions by assisting the ionization of the alkyl halide. The relative rates of reaction between 1-adamantylcarbinyl iodide and neopentyl iodide with silver salts are most informative with regards to the rearrangement step. 1-Adamantylcarbinyl derivatives have been well known as compounds that incorporate the neopentyl structure but lack the ability to rearrange because of steric bias. Indeed, the rearrangement of the 1-adamantylcarbinyl cation (V), a "strain-free" system, to the 3-homoadamantyl cation (VI) will result in energy rise of 10 kcal.[7] Rearrangement of V → VI would be much less favorable than the similar transformation II → III in the parent neopentyl system. The neopentyl rearrangement involves a simple alkyl migration because of the great driving force for conversion of a primary to a tertiary carbonium ion, and the timing of these steps is of considerable interest. It is safe to assume that the reaction of neopentyl and 1-adamantylcarbinyl derivatives should have closely similar rates if the rate-controlling step were to involve a simple ionization (to II and V, respectively), but that the neopentyl system should react faster if the methyl migration were to assist in the ionization of the departing group. We find that the relative rates of 1-adamantylcarbinyl iodide to neopentyl iodide are 2.1:1.0 and 2.0:1.0 for reactions with $AgNO_3$ and $AgClO_4$, respectively. These small rate differences between the two alkyl iodides are determined both by equilibrium and kinetic factors. However, preliminary studies show that the association constant between silver ion and neopentyl iodide is fairly similar to that between silver ion and 1-adamantylcarbinyl iodide. The above results tend to suggest that the methyl migration provides little or no assistance toward the ionization of the alkyl halide and that it probably occurs after the ionization step.



The reactions of *tert*-amyl chloride and iodide with silver nitrate in acetonitrile at 25.0° yield approximately 41% alkene, independent of the departing group. This suggests that, in the reactions of *tert*-alkyl halides with silver nitrate, the carbonium-nitrate ion pair rather than the carbonium–nitrate-silver halide quadruplet ion subsequently decomposes to form substitution and elimination products. In particular, it appears that, in the product-forming step of these *tert*-alkyl halide decompositions, the departing halogen is out of the sphere of influence of the carbocation.

The isolation of approximately the same ratio of 2-methyl-1-butene and 2-methyl-2-butene for the neopentyl iodide and *tert*-amyl halide reaction with silver salts (Table III) explicitly shows that both reactions proceed through a *tert*-amyl cation. The distribution of the two alkenes has been found to be consistent with that obtained in SN1-type reactions involving encumbered cations.[12] Although, for any given set of conditions, both alkyl halides have been found to yield the same distribution of olefins, the ratio of elimination to substitution is clearly different for neopentyl as compared with *tert*-amyl halides; yet the available evidence makes it fairly certain that the neopentyl derivative rearranges to a *tert*-amyl cation prior to its product-determining steps. Thus at 25.0°, neopentyl iodide gives a higher proportion of olefin, namely, 66.4% in comparison with 40.6% from *tert*-amyl iodide, even though the same tertiary carbonium ion is apparently formed. The difference in the ratio of the products generated by these alkyl iodides can be explained (Schemes I and II) in terms of the different structures of the product forming ion pairs or quadruplet ions.

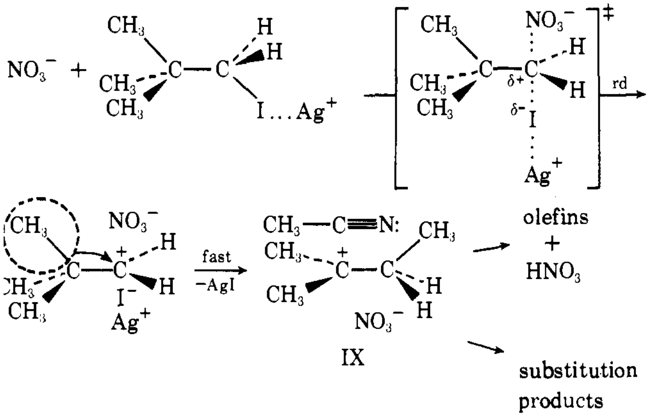
Scheme I. ***tert*-Amyl Iodide–$AgNO_3$**



With *tert*-amyl halide (Scheme I), steric bulk on the carbon atom will only permit the nucleophilic anion to assist from the rear. The manner of approach of the anion can be described in terms of a nucleophilic attack on the (RI ... Ag)$^+$ complex which assists the heterolysis of the C–I bond and produces the ion pair VIII. The collapse of these ion pairs will produce *tert*-alkyl substitution derivatives or alternatively, the anionic partner may abstract a proton to yield a mixture of alkenes.

In contrast, the reaction of neopentyl iodide with silver salts is relatively much slower. In spite of the fact that assistance from the rear should be subject to steric hindrance, the Ag^+-promoted reactions of neopentyl halides show significant anionic participation. In Scheme II, the anion is shown to assist from the least hindered side of the molecule, i.e., that opposite the slowly ionizing C–I bond. In a stepwise process, the methyl group opposite that of the ionized halogen migrates and, in so doing, positions the counterion in a poor juxtaposition for attacking the newly formed tertiary carbon but places it in a relatively more favorable position with respect to proton abstraction. Clearly, collapse of on pair IX will give less of the desired substitution product. It has been shown by several other investigators[8b-d] in their studies of deoxidation and deamination of the optically active neopentyl derivatives that rearrangement occurs stereoselectively with inversion at the deuterium-substituted carbon. This indeed is consistent with our Scheme II in which nversion would be expected at the primary carbon of the neopentyl compound.

Scheme II. Neopentyl Iodide–$AgNO_3$



In view of the fact that the reaction of neopentyl iodide with silver nitrate is quite slow, the substitution product, *ert*-amyl nitrate, has the opportunity to decompose via an E1 elimination process to a mixture containing 2-methyl-2-butene, 2-methyl-1-butene, and nitric acid (see part VII for ubsequent side reactions). In contrast, the reaction of *tert*-amyl iodide with silver nitrate in acetonitrile is quite rapid, and the products are kinetically controlled; i.e., the product atios determined during the reaction reflect the true partiioning factors associated with the *tert*-amyl nitrate ion pair. Consequently the higher percentage of elimination oberved in the reaction of the neopentyl iodide with silver nirate may in part be due to the slowness of the reaction so hat the true partitioning factors could possibly be more imilar in the two systems.

Experimental Section

Materials. The materials including $AgNO_3$, $AgClO_4$, Et_4NNO_3, and acetonitrile employed in this work have been purified and dried as described in the Experimental Section of the preceding paper.[1a] Silver trifluoroacetate (AgTFA) was prepared and ried according to the method given of Jansen and Nilson.[13] Commercially available *tert*-amyl chloride (J. T. Baker Co.) was dislled using a Vigreux column, and a constant boiling fraction, bp 5.5°, was collected (lit. bp 86.0°). *tert*-Amyl iodide was prepared rom *tert*-amyl alcohol as described by Vogel.[14] The final product as distilled under vacuum: bp 65–66° (103 mmHg); $n^{21.5}$D 4947 (lit. n^{20}D 1.4981). 1-Adamantylcarbinyl iodide was prepared from 1-adamantylcarbinol (Aldrich Chemical Co.) by the method of Landauer and Rydon.[15] The solid product was recrystallized from ethanol-water and dried under vacuum over P_2O_5, mp 53.0–54.0°.

Kinetic Measurements. All the kinetic measurements done at 75.0° reported in this paper have been carried out using the sealed bulb technique.[1a] In kinetic runs done at 25.0°, aliquots of reaction mixtures were withdrawn at regular intervals, and each sample was potentiometrically titrated. In all instances, the overall rate has been followed potentiometrically by monitoring directly $d[X^-]/dt$ or $-d[Ag^+]/dt$. Details are reported in the preceding paper.[1a]

Product Studies. Details for the measurement of acid production and of formation and distribution of alkenes, together with control runs are reported in the preceding paper.[1a]

References and Notes

(1) (a) Part VII: Y. Pocker and W.-H. Wong, preceding paper in this issue. (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.

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