Kinetics of the Reactions of t-Butyl Chloride and [²H₉]t-Butyl Chloride with Silver Salts in Acetonitrile

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Reaction of an acetonitrile solution of t-butyl chloride with silver nitrate is only slightly faster than with an equal concentration of silver perchlorate and, for concentrations of silver salt of up to 0.08M, each individual run approximates to overall second-order kinetics. The second-order rate coefficients, approximately equal for the two salts at low concentrations, increase with increasing initial concentration; the increase is more marked with the nitrate salt. Reaction with silver nitrate leads to t-butyl nitrate as well as isobutene, the subsequent elimination reaction of the nitrate ester being relatively slow compared to its rate of formation. Kinetic deuterium isotope effects for [²H₉]t-butyl chloride relative to t-butyl chloride are, for relatively low concentrations of either silver salt, essentially equal (*ca.* 2.6) to those previously observed for unimolecular decomposition. For reaction with silver nitrate, the magnitude of the isotope effect upon the partitioning between substitution and elimination is consistent with attack upon an intermediate carbonium ion. The pathway is best considered as approximating to the Hughes–Ingold S_N1Ag⁺- (plus $E1$Ag⁺) mechanism, with the slightly faster reaction with the moderately nucleophilic nitrate salt reflecting a partial diversion of an intermediate R⁺Cl⁻Ag⁺ ion-triplet away from internal return of chloride ion.

REACTIONS in acetonitrile of silver nitrate with a variety of primary,[1-3] secondary,[1,3] and allyl halides[4] have been found to follow closely a 2½-order kinetic equation, unit order in organic halide and 1½-order in silver nitrate. In several instances it has been shown that these organic halides react appreciably faster with silver nitrate than

with silver perchlorate[1,4,5] and it has been suggested that both electrophilic and nucleophilic assistance operate in the rate-determining step.[1,3,4] In acetonitrile containing pyridine, t-butyl chloride undergoes elimination reaction by first-order kinetics[6] and it is possible

¹ G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.,* 1960, **82,** 704.
² F. G. Donnan and H. E. Potts, *J. Chem. Soc.,* 1910, **97,** 882; for a reassessment of these data see ref. 3.

³ Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.,* 1965, **87,** 4760.
⁴ D. N. Kevill and L. Held, *J. Org. Chem.,* 1973, **38,** 4445.
⁵ Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.,* 1965, **87,** 4771.
⁶ D. N. Kevill and J. E. Dorsey, *Chem. and Ind.,* 1967, 2174.

that reaction of this substrate with silver nitrate might, similarly, involve only electrophilic assistance in the rate-determining step [7] (S_N1Ag^+ and/or $E1Ag^+$ reaction [8]). In the presence of chloride ion, t-butyl chloride in acetonitrile does show (superimposed upon the unimolecular component) an appreciable bimolecular contribution to the elimination reaction and the moderately nucleophilic nitrate ion [3] could act in like manner upon the pre-formed alkyl halide–silver ion complex.[9]

The present investigation gives consideration to whether the reaction of silver nitrate with t-butyl chloride in acetonitrile follows the $2\frac{1}{2}$-order kinetic equation, previously observed with other organic halides, or a lower order (possibly second-order) form which would be predicted in the absence of nucleophilic assistance of the rate-determining step. Other aspects of the investigation include determination of the relative rates of reaction with silver nitrate and silver perchlorate, determination of the product distribution for reaction with silver nitrate (t-butyl nitrate has previously been shown to be only moderately reactive in acetonitrile),[10] determination of kinetic deuterium isotope effects for reaction with both silver nitrate and silver perchlorate, and determination of deuterium isotope effects upon product distribution for reaction with silver nitrate. Consideration is given to possible reaction mechanisms.

EXPERIMENTAL

Acetonitrile (Mallinckrodt, Nanograde) was purified as described previously.[11] t-Butyl chloride (Eastman) was purified by fractional distillation and [$^2H_9$]t-butyl chloride (isotopic purity >99%) was used as supplied by Merck, Sharpe and Dohme. Silver perchlorate (G. F. Smith Chemical Co., anhydrous) was dried at 110° and allowed to cool in a desiccator, acetonitrile was then directly added and the concentration of the solution determined by potentiometric titration of a portion against a standard solution of potassium chloride using acetone (20 ml) containing N-HNO_3 (1 ml) (to increase the conductivity) as diluent, a silver-wire electrode, and a potassium nitrate–agar bridge to a calomel reference electrode. Tetraethylammonium nitrate was prepared by neutralization of the hydroxide with nitric acid, evaporation to dryness under reduced pressure, recrystallization from acetone, and drying at 60° under vacuum.

Kinetic Measurements.—With the exception of silver perchlorate (see above) stock solutions of reactants were prepared by weighing into volumetric flasks and filling to the mark with acetonitrile at the appropriate temperature. Solutions were then made by appropriate dilution of these stock solutions with acetonitrile. After temperature equilibration, a portion (2 ml) was transferred into acetone (20 ml) cooled to −78° and, after some warming of the solution, potentiometric titration of unprecipitated silver ion was carried out, in the manner indicated above. At appropriate intervals, further portions (2 ml) were removed and titrated.

When acid development was also followed, portions (2 ml)

were transferred into acetone (20 ml), containing Lacmoid (Resorcinol Blue) as indicator and maintained at −78°, and titrated against an appropriate standard solution of sodium methoxide in methanol.

Two illustrative runs, in which both the rate of silver chloride precipitation and the rate of acid production were measured, are given in Table 1.

TABLE 1

Illustrative runs for reactions of t-butyl chloride with silver salts in acetonitrile at 35.0°

(a) 2 ml portions; [t-C_4D_9Cl] 0.071 9M; [$AgNO_3$] 0.160M; titres (ml) of 0.040 0N-KCl and 0.010 1N-NaOMe

t/min	0.00	20.00	40.45	59.85	80.50
Titre (KCl)	8.05	7.75	7.50	7.28	7.03
Titre (NaOMe) [a]	0.06	0.42	0.74	1.06	1.36
$10^4 k_2$/l mol^{-1} s^{-1}		4.53	4.34	4.32	4.53
F_E		0.33	0.33	0.34	0.33
t/min	100.00	119.90	140.15	160.36	182.55
Titre (KCl)	6.90	6.71	6.50	6.43	6.24
Titre (NaOMe) [a]	1.60	1.81	2.03	2.26	2.49
$10^4 k_2$/l mol^{-1} s^{-1}	4.26	4.36	4.59	4.28	4.47
F_E	0.34	0.34	0.33	0.35	0.34

(b) 2 ml portions; [Bu^tCl] 0.080 0M; [$AgClO_4$] 0.040 0M; titres (ml) of 0.010 0N-KCl and 0.009 50N-NaOMe

t/min	0.00	29.92	60.25	89.74	119.87
Titre (KCl)	7.46		7.00	6.82	6.60
$10^4 k_2$/l mol^{-1} s^{-1} [b]			2.31	2.20	2.27
Titre (NaOMe) [a]	0.10	0.40	0.66		0.88
$10^4 k_2$/l mol^{-1} s^{-1} [c]		2.46	2.39		2.25
t/min	149.74	179.70	210.24	290.49	
Titre (KCl)	6.39	6.26	6.08	5.58	
$10^4 k_2$/l mol^{-1} s^{-1} [b]	2.31	2.19	2.20	2.31	
Titre (NaOMe) [a]	1.33	1.55	1.72	2.23	
$10^4 k_2$/l mol^{-1} s^{-1} [c]	2.30	2.31	2.25	2.27	

[a] Portions taken 0.50 min after reported times. [b] Based on silver chloride precipitation. [c] Based on acid production.

RESULTS

(i) *Reaction of t-Butyl Chloride with Silver Nitrate.*—A study was made at 35.0° of the reaction between t-butyl chloride (0.04—0.16M) and silver nitrate (0.005—0.16M); brief studies were also made at 25.0 and 45.0°. For each individual run, it was found that the overall kinetics for silver chloride precipitation were very close to second order. The average values for the second-order rate coefficients were found to be independent of the initial t-butyl chloride concentration and to drift upwards as the concentration of silver nitrate was increased.

For several runs, the extent of acid development, corresponding to the elimination reaction, was simultaneously determined and, by comparison with the overall extent of reaction, the fraction of overall reaction proceeding with elimination was determined. Although t-butyl nitrate [12] formed in the substitution process undergoes subsequent elimination, the rate of indirect elimination *via* the nitrate ester is sufficiently slow [10] for determination during the initial stages of reaction to be an accurate measure of the extent of elimination for the reaction of t-butyl chloride with silver nitrate. Reported values were obtained by extrapolation of the very slowly increasing values (see example in Table 1) to zero time.

[7] N. Kornblum and D. E. Hardies, *J. Amer. Chem. Soc.*, 1966, **88**, 1707.

[8] See, for example, C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, 1969, 2nd edn., pp. 479—483.

[9] D. N. Kevill, V. V. Likhite, and H. S. Posselt, *J.C.S. Perkin II*, 1975, 911.

[10] D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc. (B)*, 1969, 366.

[11] D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, 1969, **34**, 1985.

[12] G. R. Lucas and L. P. Hammett, *J. Amer. Chem. Soc.*, 1942, **64**, 1928.

For the reaction of 0.08M-t-butyl chloride with 0.04M-silver nitrate at 35.0°, a study was made of the effect upon both overall kinetics and the fraction of reaction proceeding

TABLE 2

Averaged integrated second-order rate coefficients for precipitation of silver chloride in the reaction of t-butyl chloride with silver nitrate, in acetonitrile at various temperatures and initial fraction of reaction proceeding with acid formation (F_E)

$T/°C$	[Bu^{t}Cl]/M	[AgNO$_3$]/M	$10^4 k_2$ ^{a}/l mol^{-1} s^{-1}	F_E
35.0	0.080 0	0.005 0	1.96 ± 0.19	
	0.080 0	0.010 0	2.25 ± 0.04	
	0.080 0	0.020 0	2.89 ± 0.03	
	0.080 0	0.040 0	4.45 ± 0.07 ^{b}	0.50 ^{c}
	0.040 0	0.080 0	5.64 ± 0.13	
	0.080 0	0.080 0	5.87 ± 0.24	
	0.160 0	0.080 0	5.84 ± 0.20	0.39
	0.080 0	0.160 0	9.69 ± 0.17	0.37
25.0	0.080 0	0.040 0	1.35 ± 0.10	
	0.040 0	0.080 0	1.79 ± 0.20	
	0.080 0	0.080 0	1.77 ± 0.14	0.34
45.0	0.080 0	0.040 0	11.5 ± 0.2	
	0.080 0	0.080 0	15.6 ± 0.3	0.43

^{a} With associated standard deviations. ^{b} In the presence of 0.040,0, 0.080 0, and 0.160M-tetraethylammonium nitrate, initial values are increased to 4.8, 5.5, and 5.9 × 10^{-4} l mol^{-1} s^{-1}, respectively. ^{c} In the presence of 0.040 0, 0.080 0, and 0.160M-tetraethylammonium nitrate, values are decreased to 0.437, 0.402, and 0.345, respectively.

with elimination of added tetraethylammonium nitrate (0.04—0.16M).

Results are reported in Table 2.

(ii) *Reaction of t-Butyl Chloride with Silver Perchlorate.—* A study was made at 35.0° of the reaction of t-butyl

controlled product ratios. This does have the advantage that the overall rate of reaction can also be followed in terms of acid formation and in two instances the overall kinetics were followed by both techniques.

The results of these studies are in Table 3.

(iii) *Deuterium Isotope Effects in the Reactions of t-Butyl Chloride with Silver Nitrate and Silver Perchlorate.—*Dual experiments with 0.071 9M-t-butyl chloride or [^{2}H$_9$]t-butyl chloride were carried out simultaneously and with a

TABLE 3

Averaged integrated second-order rate coefficients for precipitation of silver chloride in the reaction of t-butyl chloride with silver perchlorate, in acetonitrile at 35.0°

[Bu^{t}Cl]/M	[AgClO$_4$]/M	$10^4 k_2$ ^{a}/l mol^{-1} s^{-1}
0.080 0	0.005 0	1.68 ± 0.03 ^{b}
0.080 0	0.010 0	2.03 ± 0.10
0.080 0	0.020 0	1.97 ± 0.11
0.080 0	0.040 0	2.26 ± 0.06 ^{c}
0.040 0	0.080 0	3.01 ± 0.10
0.080 0	0.080 0	2.95 ± 0.23
0.160 0	0.080 0	3.15 ± 0.16

^{a} With associated standard deviations. ^{b} In terms of acid formation, a value of 1.56 (±0.10) × 10^{-4} l mol^{-1} s^{-1} was obtained. ^{c} In terms of acid formation, a value of 2.32 (±0.10) × 10^{-4} l mol^{-1} s^{-1} was obtained.

series of concentrations of silver nitrate or silver perchlorate (0.01—0.16M) at 35.0°. For both silver salts, the overall extent of reaction was followed in terms of silver chloride precipitation and, for silver perchlorate, it was also followed in terms of acid production. For silver nitrate, acid production relative to silver chloride precipitation

TABLE 4

Averaged second-order rate coefficients for silver chloride precipitation ^{a} in the reaction of 0.071 9M-t-butyl chloride or 0.071 9M-[^{2}H$_9$]t-butyl chloride with silver nitrate in acetonitrile at 35.0°, and corresponding initial fractions of reaction proceeding with acid formation (F_E^H and F_E^D)

[AgNO$_3$]/M	$10^4 k_2^H$/l mol^{-1} s^{-1}	$10^4 k_2^D$/l mol^{-1} s^{-1}	F_E^H	F_E^D	P^H/P^D ^{b}	k_2^H/k_2^D ^{a}
0.010 0	2.43 ± 0.07	0.908 ± 0.055	0.61			2.68 ± 0.18
0.020 0	2.98 ± 0.11	1.14 ± 0.07	0.59	0.51	1.35	2.62 ± 0.19
0.040 0	4.48 ± 0.20	1.55 ± 0.09	0.50	0.48	1.10	2.89 ± 0.22
0.060 0	5.06 ± 0.17	1.94 ± 0.14	.0.46	0.38	1.39	2.61 ± 0.21
0.160 0	9.85 ± 0.28	4.44 ± 0.09	0.37	0.32	1.21	2.22 ± 0.08

^{a} With associated standard deviations. ^{b} $P^H = F_E^H/F_S^H$ and $P^D = F_E^D/F_S^D$, F_S (fraction of reaction proceeding with substitution) $= 1 - F_E$; average value for P^H/P^D is 1.26 ± 0.12.

TABLE 5

Averaged second-order rate coefficients ^{a} for reaction of 0.071 9M-t-butyl chloride or [^{2}H$_9$]t-butyl chloride with silver perchlorate in acetonitrile at 35.0°

[AgClO$_4$]/M	AgCl Precipitation			Acid production		
	$10^4 k_2^H$/l mol^{-1} s^{-1}	$10^4 k_2^D$/l mol^{-1} s^{-1}	k_2^H/k_2^D ^{a}	$10^4 k_2^H$/l mol^{-1} s^{-1}	$10^4 k_2^D$/l mol^{-1} s^{-1}	k_2^H/k_2^D ^{a}
0.009 50	1.90 ± 0.06	0.691 ± 0.019	2.75 ± 0.12	1.75 ± 0.14	0.712 ± 0.016	2.46 ± 0.21
0.019 9	2.03 ± 0.06	0.765 ± 0.033	2.65 ± 0.14	1.96 ± 0.11	0.667 ± 0.051	2.94 ± 0.28
0.039 8	2.20 ± 0.05	0.919 ± 0.053	2.39 ± 0.14	2.17 ± 0.06	0.985 ± 0.026	2.20 ± 0.09
0.079 6	2.90 ± 0.10	1.30 ± 0.03	2.23 ± 0.10	3.16 ± 0.18	1.37 ± 0.11	2.31 ± 0.24

^{a} With associated standard deviations.

chloride (0.04—0.16M) with silver perchlorate (0.005—0.16M). For concentrations up to and including 0.08M, analysis of each individual run in terms of silver chloride precipitation was best carried out in terms of second-order rate coefficients. In this system, possible substitution products (t-butyl perchlorate or N-t-butylacetonitrilium ion) will be highly reactive in subsequent elimination reaction and it is not possible to determine kinetically

gave a measure of the partitioning between elimination and substitution.

Results for reaction with silver nitrate are reported in Table 4 and for reaction with silver perchlorate in Table 5.

DISCUSSION

In terms of overall kinetics, values for the integrated second-order rate coefficients, although essentially

constant throughout an appreciable extent of each individual run, drift upwards from run to run as the concentration of silver salt is increased (Tables 2 and 3). Above 0.08M-silver perchlorate, the integrated second-order rate coefficients drifted downwards throughout the

Second-order rate coefficients for reaction of t-butyl chloride with silver nitrate (O) or silver perchlorate (□) in acetonitrile at 35.0°

run, indicating the incursion of terms of higher kinetic order. Similarly, the kinetics of silver-ion assisted solvolysis of t-butyl chloride in ethanol have been related to both second- and third-order kinetic terms.[13]

The kinetic pattern of the reaction with silver perchlorate parallels that previously observed with secondary

of primary, secondary, and allyl halides but is of relatively minor importance in the reactions of t-butyl chloride. Addition of tetraethylammonium nitrate, at concentrations of up to 0.16M, leads to only modest increases (<30%) in the second-order rate coefficients for reaction with 0.04M-silver nitrate. At low concentrations, very similar rates of reaction with silver perchlorate and silver nitrate are observed. As the concentrations are increased, the second-order rate coefficients increase with both salts but a greater increase is observed with the nitrate, at 0.08M the nitrate reacts about twice as fast (Figure). This is consistent with some nucleophilic assistance by the nitrate ion (silver perchlorate is more dissociated than an equal concentration of silver nitrate[3] but considerably less than in previously studied systems; for example,[4] at 0.04M-silver nitrate reacts with allyl bromide $ca.$ 1 600 times faster than silver perchlorate and, at 0.03M, the corresponding value for 2-bromo-octane is 80. It is quite possible that this nucleophilic assistance occurs at an ion-triplet $(R^+Cl^-Ag^+)$ stage, such that internal return of chloride ion[14] is to some degree prevented by interaction with a nitrate ion. A generalized presentation of possible reaction pathways is given in the Scheme. The above suggestion would correspond to reactions (4) and (5) competing with (3).

This behaviour is consistent with that previously proposed for non-electrophilically assisted bimolecular substitution and elimination reactions of tertiary α-halogenated ketones.[15] Recently, an alternative approach has been taken towards bimolecular attack at

Scheme

halides.[5] With silver nitrate, the good correlation using second-order rate coefficients is in contrast to the $2\frac{1}{2}$-order observed for reactions of primary,[5] secondary,[3,5] and allyl[4] halides with this salt; for reaction with 2-bromo-octane, it was shown that the additional 1/2-order relates to the concentration of nitrate ion, suggesting nucleophilic assistance is an important factor in reactions

tertiary structures.[16] For attack upon γ-p-tolylsulphonyl-substituted tertiary allylic systems, it has been proposed that the rate-determining step involves attack of the solvated nucleophile upon the unactivated substrate with direct formation of a solvated ion-triplet which then, in subsequent fast steps, proceeds to products; a major rate-limiting factor in this mechanism

[13] I. V. Kozhevnikov and E. S. Rudakov, *Reakts. spos. org. Soedinenii*, 1971, **8**, 517 (*Chem. Abs.*, 1972, **76**, 33493).
[14] D. N. Kevill and C. R. Degenhardt, *J.C.S. Chem. Comm.*, 1974, 662.

[15] D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 1961, 252; *J. Amer. Chem. Soc.*, 1961, **83**, 3815.
[16] (a) F. G. Bordwell and G. A. Pagani, *J. Amer. Chem. Soc.*, 1975, **97**, 118; (b) F. G. Bordwell and T. G. Mecca, *ibid.*, pp. 123, 127; (c) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *ibid.*, p. 132.

is the accompanying solvent reorganization.* It is of interest that both these two types of substrates [15,16] have the tertiary structure modified by insertion of election-withdrawing substituents and it has been suggested that they assist bimolecular attack involving ion-triplet formation by inhibiting dissociation to a greater degree than ionization.[16]

At low concentrations of silver salt, reaction (5) will be the dominant pathway by which the ion-triplet progresses to products but as the concentration of the reasonably nucleophilic nitrate [18] increases contributions from reaction (4) can become important. Perchlorate is much less nucleophilic [18,19] and presumably reaction (4) is of less importance for its silver salt. For silver perchlorate, the increase in second-order rate coefficient with increasing concentration of silver salt is almost certainly due to effects involving the silver ion.[9] Such effects may well, in conjunction with nitrate ion participation, lead to part of the increase observed with silver nitrate.

For silver perchlorate, the overall extent of reaction can be followed either in terms of acid formation or silver-ion precipitation. For silver nitrate, reaction proceeds in part with formation of t-butyl nitrate, without accompanying acid formation; determination of both acid formation and silver-ion precipitation allows one to establish the fraction of overall reaction proceeding with elimination. At 35.0, the fraction of reaction proceeding with elimination falls from 0.50 to 0.37 as the concentration of silver nitrate increases from 0.04 to 0.16M; similarly, additions of tetraethylammonium nitrate favour substitution relative to elimination (Table 2). This is consistent with pathways (7), (10), and (11), leading to elimination, being reduced in importance as the concentration of anionic nucleophile is increased, leading to increased importance for the pathway involving (4). The reason that (7) is excluded as a pathway leading to appreciable amounts of substitution is the observation that, in aprotic solvents, t-butyl bromide gives appreciable amounts of substitution product only in the presence of powerful nucleophiles.[20] With azide ion in dimethylformamide as much as 20% substitution can be observed but with chloride ion in either acetone or dimethylformamide only ca. 5% substitution is observed.[21] Similar results have been observed with other tertiary halides and sodium azide in dimethyl-

formamide.[22] These reactions can be formulated as proceeding through a Y^-R^+ intermediate identical to that formed in (7). Elimination is favoured (as is usually the case) by an increase in temperature. This is illustrated in Table 2 for 0.08M-silver nitrate.

The observation of appreciable t-butyl nitrate formation is consistent with its synthesis by a heterogeneous reaction between t-butyl bromide and powdered silver nitrate in an inert solvent.[23] Under homogeneous conditions, Hoffmann[24] has shown that, at $-30°$, t-butyl bromide reacts rapidly with an acetonitrile solution of silver toluene-p-sulphonate to give ca. 70% of the substitution product, even although toluene-p-sulphonate is a relatively weak nucleophile.[18] While the lower temperature will favour substitution, this effect would be expected to be more than balanced out by the low nucleophilicity relative to chloride or azide. Hoffmann also found that silver toluene-p-sulphonate reacted ten times faster than silver tetrafluoroborate (at 0.035M). At identical concentration and at 35°, silver nitrate reacts only twice as fast as silver perchlorate; it should be emphasized, however, that there is a considerable temperature difference between the two sets of measurements.

The tendency for silver salts to favour substitution with the anion of the silver salt has also been observed when the competing reaction is not elimination but solvolytic substitution. For example, 1-adamantyl toluene-p-sulphonate solvolyses in 0.15M ethanolic tetraethylammonium chloride without concurrent formation of 1-adamantyl chloride[17] but 1-adamantyl halides react with even lower concentrations of silver nitrate in ethanol with formation of predominantly 1-adamantyl nitrate.[25] Probably the best explanation for the tendency of silver-ion assisted reactions to proceed with formation of appreciable quantities of the anionic substitution product under conditions where reactions in the absence of electrophilic assistance proceed with predominant elimination or solvolytic substitution product is the previously postulated intermediacy in the silver-ion assisted reactions of clusters containing silver ions, counterions, carbonium ions, and halide ions [3,9] with the counterion situated favourably relative to the carbonium ion for collapse to substitution product.

It is of interest that Miller[26] has found zinc chloride assisted in the formation of tertiary azides from tertiary halides by heterogeneous reaction with electrophilic

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* It has been stated [16c] that one piece of evidence inconsistent with solvolytic (nucleophilic) rate-determining attack upon tertiary structures is the observation, for γ-p-tolylsulphonyl-$\alpha\alpha$-dimethylallyl methanesulphonate of a $[k(H_2O-ROH)/k(AcOH)]_T$ value of 0.82. This is on the reasonable assumption that in aqueous ethanol and acetic acid of equal Grunwald–Winstein ionizing power (Y value), any nucleophilic participation will lead to a greater rate increase in the more nucleophilic aqueous ethanol. The prediction of unity for limiting ionization was based on t-butyl chloride solvolysis. A much more reasonable model for limiting ionization of sulphonate esters is 1-adamantyl toluene-p-sulphonate which exhibits a $[k(H_2O-ROH)/k(AcOH)]_T$ value of 0.20.[17] On this basis, a value of 0.82 suggests nucleophilic participation and it is consistent with the proposed interpretation.

[17] D. N. Kevill, K. C. Kolwyck, and F. L. Weitl, J. Amer. Chem. Soc., 1970, 92, 7300.

[18] J. Hine, ' Physical Organic Chemistry,' McGraw-Hill, New York, 1962, 2nd edn., pp. 160—161.

[19] For a comment on the nucleophilicity of perchlorate ion in aprotic solvents, see D. J. Raber, J. M. Harris, and P. v. R. Schleyer, 'Ions and Ion Pairs in Organic Reactions,' ed. M Szwarc, Wiley–Interscience, New York, 1974, vol. 2, p. 334.

[20] A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, J. Amer. Chem. Soc., 1972, 94, 2228.

[21] D. Cook and A. J. Parker, J. Chem. Soc. (B), 1968, 142.

[22] R. A. Abramovitch and E. P. Kyba, J. Amer. Chem. Soc., 1974, 96, 480.

[23] J. W. Baker and D. M. Easty, J. Chem. Soc., 1952, 1193.

[24] H. M. R. Hoffmann, J. Chem. Soc., 1965, 6748.

[25] D. N. Kevill and V. M. Horvath, Tetrahedron Letters, 1971, 711.

[26] J. A. Miller, Tetrahedron Letters, 1975, 2959.

zinc halide and nucleophilic sodium azide in carbon disulphide. For example, t-butyl chloride gave a 96% yield of t-butyl azide. It was not established, however, whether the products resulted from kinetic or thermodynamic control and an elimination–addition route appears possible.

Overall kinetic deuterium isotope effects for the second-order rate coefficients for reaction with t-butyl chloride or $[^2H_9]$t-butyl chloride, at 35.0°, are very similar for either silver nitrate or silver perchlorate (Tables 4 and 5) and at the lower silver salt concentrations, within experimental error, identical to those observed for the unimolecular dehydrochlorination at 45° (2.62 ± 0.02).[6] In contrast, chloride-ion promoted bimolecular dehydrochlorination exhibited [11,27] a value of 3.81 ± 0.21. This is consistent with the view that the rate-determining process involves primarily silver-ion assisted ionization of the carbon–halogen bond, with the possibility of return from within an ion-triplet [14] being partially circumvented by intervention of nitrate ion. At higher concentrations, of either silver nitrate or silver perchlorate, there was evidence for a fall off in the value of the deuterium isotope effect. This may reflect the influence of additional silver ions upon the rate-determining step.[9,13,28] In hydroxylic (hydrogen-bonding) solvents the value of k_H/k_D is somewhat less than in acetonitrile;[29-32] for example, a corresponding value of 2.22 has been estimated [6] from data [32] in 1 : 1 ethanol–water. Possibly, the influence of additional silver ions in acetonitrile can be equated to hydrogen-bonding influences in hydroxylic solvents.

For reaction with silver nitrate, it is also possible to consider the deuterium isotope effect upon the partitioning between substitution and elimination. Over a range of silver nitrate concentrations of 0.01—0.16M, although the actual fractions of substitution rise with increasing concentration, it is not possible to observe any trend in the P^H/P^D value (1.26 ± 0.12), where $P_H = F_E^H/F_S^H$ and $P_D = F_E^D/F_S^D$ and F_E and F_S are fractions of substitution and elimination for hydrogen (H) or deuterium (D). If it is accepted that the products are formed by attack on an intermediate carbonium ion then the planar (or near-planar) geometry around the carbonium carbon should lead to low isotope effects for the fast bimolecular substitution process and, if the isotope effect upon this process is assumed to be negligible, then the P_H/P_D values can be identified with the weighted β-deuterium isotope effect for bimolecular elimination (promoted by either nitrate ion or solvent) from the carbonium ion. The value of 1.26 corresponds in turn to a value of 1.08 per CD_3 group. This value is consistent with those previously proposed [33] for this type of process.

[27] For a discussion of isotope effects in elimination reactions, see R. A. More O'Ferrall, ' Elimination Reactions in Solution,' in ' The Chemistry of the Carbon–Halogen Bond,' ed. S. Patai, Wiley–Interscience, New York, 1973.

[28] E. S. Rudakov, V. V. Zamashchikov, and R. I. Rudakova, Org. Reactivity, 1970, 7, 363.

[29] K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, Canad. J. Chem., 1960, 38, 2171.

[30] V. J. Shiner, jun., B. L. Murr, and G. Heinemann, J. Amer. Chem. Soc., 1963, 85, 2413.

[31] G. J. Frisone and E. R. Thornton, J. Amer. Chem. Soc., 1964, 86, 1900.

[32] L. Hakka, A. Queen, and R. E. Robertson, J. Amer. Chem. Soc., 1965, 87, 161.

[33] B. L. Murr and M. F. Donnelly, J. Amer. Chem. Soc., 1970, 92, 6686, 6688.