Kinetics and Mechanism of the Reaction of Methyl Iodide with Silver Perchlorate in Nitromethane [1]

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The initially homogeneous reaction of silver perchlorate with methyl iodide in nitromethane yields, together with a precipitate of silver iodide, *ca.* 80% methyl perchlorate, accompanied by an unidentified amorphous red solid. For a constant initial concentration of silver perchlorate, the initial reaction rate increases less than linearly with increasing initial methyl iodide concentration and the data can be analysed in terms of Michaelis–Menton type kinetics, strong evidence for the intermediate formation of an alkyl halide–silver ion complex. For a constant initial concentration of methyl iodide, the initial reaction rate increases more than linearly with increasing initial silver perchlorate concentration and the order in silver perchlorate increases from close to unity at low concentrations to *ca.* 2·7 at 0·22M. Added tetraethylammonium perchlorate leads to relatively modest rate increases and does not influence the distribution of products. Possible reaction mechanisms are discussed and related to previously proposed non-electrophilically assisted mechanisms for nucleophilic substitution.

Silver ion assistance to nucleophilic substitution and elimination reactions of alkyl halides has been known for many years. Some of the earlier kinetic studies were performed upon systems of this type, including studies of the reactions of ethyl iodide with silver nitrate in ethanol [2,3] and in acetonitrile.[4] After establishment of the duality of mechanism for nucleophilic substitution and elimination, the reactions were considered in terms of a unimolecular (ionization) process assisted by a silver ion, *i.e.*, for substitution, an S_N1Ag^+ reaction.[5] It has now been established that many of these reactions proceed with simultaneous electrophilic and nucleophilic assistance and opinions have varied on whether the reactions should be considered as termolecular [6,7] or as a bimolecular attack upon an alkyl halide–silver ion complex.[8-11] Further, if reactions with rate-determining nucleophilic assistance proceed through an alkyl halide–silver ion complex, it appears probable that many, if not all, of the S_N1Ag^+ reactions also involve such a complex.

In addition to the work of Donnan and Potts,[4] studies of the reactions of silver nitrate in acetonitrile with alkyl halides,[6-9] allyl halides,[11] and chloroformate esters [12,13] have been made. Acetonitrile is a good solvent for many silver salts but the extensive solvation of the silver ion, which supports the high solubility [probably with the formation of discrete $Ag(CH_3CN)_2^+$ species [8a]] also reduces its electrophilicity.

A few silver salts, such as the perchlorate, are soluble in other organic solvents and kinetic studies have been carried out in benzene of the relatively rapid reactions with methyl iodide [14] to give methyl perchlorate,[15,16] with 1-methylheptyl bromide to give a mixture of 1-methylheptyl perchlorate and octenes,[8d] and with alkyl chloroformates to give, in addition to alkyl perchlorates and alkenes, alkylbenzenes.[17] Ion pair association, which occurs in benzene solutions of silver perchlorate [18,19] is no doubt responsible for the observed complex kinetics.

Silver perchlorate also has appreciable solubility in nitromethane and conductivity measurements indicate appreciable ionic dissociation.[20] Accordingly, we considered it worthwhile to utilize this solvent for an investigation of the kinetics of the reaction of silver perchlorate with methyl iodide. Although t-butyl perchlorate is converted into a polymer of molecular weight 700—800 and approximate empirical formula C_7H_6 in

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[2] A. K. Burke and F. G. Donnan, *J. Chem. Soc.*, 1904, **85**, 555.

[3] F. G. Donnan and A. K. Burke, *Z. phys. Chem.*, 1909, **69**, 148.

[4] F. G. Donnan and H. E. Potts, *J. Chem. Soc.*, 1910, **97**, 882.

[5] See, for example, C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1953, pp. 357—360.

[6] G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, 1960, **82**, 704.

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

[8] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, 1965, **87** (*a*) 4760; (*b*) 4771; (*c*) 4778; (*d*) 5060.

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

[10] R. Huq, *J.C.S. Faraday I*, 1972, 1824.

[11] D. N. Kevill and L. Held, *J. Org. Chem.*, 1973, **38**, 4445.

[12] D. N. Kevill and G. H. Johnson, *J. Amer. Chem. Soc.*, 1965, **87**, 928.

[13] D. N. Kevill and G. H. Johnson, *Chem. Comm.*, 1966, 235.

[14] M. F. Redies and T. Iredale, *J. Phys. Chem.*, 1944, **48**, 224.

[15] H. Burton and P. F. G. Praill, *Chem. and Ind.*, 1951, 939.

[16] D. N. Kevill and H. S. Posselt, *Chem. Comm.*, 1967, 438.

[17] D. N. Kevill, W. A. Reis, and J. B. Kevill, *Tetrahedron Letters*, 1972, 957.

[18] A. E. Hill, *J. Amer. Chem. Soc.*, 1921, **43**, 254.

[19] F. M. Batson and C. A. Kraus, *J. Amer. Chem. Soc.*, 1934, **56**, 2017.

[20] D. M. Murray-Rust, H. J. Hadow, and H. Hartley, *J. Chem. Soc.*, 1931, 215.

nitromethane,[21] primary alkyl perchlorates have been shown to be quite stable.[22] Reaction of alkyl perchlorates with nitromethane have been found only under extreme conditions; for instance, after seven days at 100°, tris-*p*-methoxyphenylmethyl perchlorate gave a moderate yield of $NO_2CH_2C(C_6H_4OCH_3\text{-}p)_3$.[23] It was expected that the kinetic pattern might be less complex than in benzene and that methyl perchlorate would be formed in good yield.

EXPERIMENTAL

Nitromethane was dried and purified as described by Olah *et al.*[24] Methyl iodide was washed twice with concentrated sulphuric acid and four times with concentrated aqueous sodium hydrogen carbonate; it was then dried ($CaSO_4$) for two days and distilled. Silver perchlorate (G. F. Smith Chemical Co.) was dried at 110° for two days and allowed to cool over anhydrous calcium sulphate; solutions in nitromethane, made by rapid addition of the anhydrous salt to the solvent, were standardized by potentiometric titration against aqueous potassium iodide. Tetraethylammonium perchlorate was prepared by addition of 70% perchloric acid to 25% tetraethylammonium hydroxide until the solution was just acid to litmus and the precipitated salt was filtered off and recrystallized from nitromethane.

Kinetic Measurements.—Portions of stock solutions of methyl iodide, silver perchlorate, and (when appropriate) tetraethylammonium perchlorate were diluted to 50 ml to give a reactant solution of the required composition. At intervals, portions (3 ml) were removed and quenched in acetone (40 ml) cooled to *ca.* −10° in methanol–ice. *N*-Nitric acid (1 ml) was added (to increase the conductivity) and the extent of reaction, in terms of consumption of silver ion, was determined by potentiometric titration against standard aqueous potassium iodide, by using a silver-wire electrode and a potassium nitrate–agar bridge with a calomel reference electrode.

TABLE 1

Sample kinetic runs for reactions of silver perchlorate and methyl iodide in nitromethane

A $[CH_3I]$ 0·112M; [a] $[AgClO_4]$ 0·111M; [a] titres, ml of 0·0369N-KI and ml of 0·00300N methanolic $NaOCH_3$

t/min	0	20	40	60	80	100	120	140	165	180	200	220
Titre(KI)	8·89	7·77	6·91	6·25	5·73	5·30	4·94	4·62	4·33	3·96	3·54	3·12
$10^5k_1/s^{-1}$		11·2	10·5	9·8	9·2	8·6	8·2	7·8	7·3	7·5	7·7	7·9
Titre($NaOCH_3$)	0·08				6·45				9·50			12·60
Acid (%)					17				17			18

B $[CH_3I]$ 0·112M; [a] $[AgClO_4]$ 0·0276M; [a] titres, ml of 0·0185N-KI and ml of 0·00300N methanolic $NaOCH_3$

t/min	0	60	90	120	150	180	210	240	270	300	330
Titre(KI)	4·48	4·18	4·02	3·92	3·84	3·70	3·58	3·48	3·34	3·24	3·11
$10^5k_1/s^{-1}$		1·93	2·01	1·85	1·71	1·86	1·78	1·76	1·81	1·80	1·96
Titre($NaOCH_3$)	0·02			0·50				1·14			1·16
Acid (%)				14				18			14

C $[CH_3I]$ 0·112M; [a] $[AgClO_4]$ 0·000867M; [a] titres, ml of 0·000249N-KI

t/min	0	60	120	180	240	300	360	420	480	540	600	660
Titre(KI)	9·03	8·78	8·50	8·20	7·90	7·63	7·39	7·23	6·87	6·65	6·39	6·10
$10^5k_1/s^{-1}$		0·83	0·87	0·88	0·95	0·94	0·94	0·89	0·97	0·95	0·97	1·00

[a] Initial concentrations.

Alternatively, portions (3 ml) were also pipetted into acetone (40 ml) saturated with lithium chloride (to convert methyl perchlorate into relatively unreactive methyl chloride) and containing Resorcinol Blue (Lacmoid) as indicator. The acid developed was then determined by titration against a standard solution of sodium methoxide in methanol. Identical values were obtained when the portions were added to *ca.* 0·5 g of solid tetraethylammonium bromide, lithium chloride, or tetramethylammonium iodide before addition of the acetone and titration.

Three illustrative kinetic runs are given in Table 1.

Product Studies.—Because of the extremely explosive properties of simple alkyl perchlorates,[25,26] no attempt was made to isolate methyl perchlorate from the reaction mixture. The titrations indicated methyl perchlorate to be formed in 80—85% yield, accompanied by 15—20% of material (which led to a dark red solution) developed concurrent with acid.

In a typical product study, an ampoule containing silver perchlorate (9·40 g) was placed in a three-necked flask and the flask was purged with dry air (molecular sieves) for *ca.* 30 min. During this time, nitromethane (225 ml) was added and the ampoule was then broken under the solvent level. Under dry air, methyl iodide (2·96 ml; 5% excess) was added. The mixture was stirred for several hours with occasional shaking to avoid separation of the more volatile methyl iodide by condensation on the walls of the container. Silver iodide was filtered off to leave a dark red solution.

Titration of a portion indicated *ca.* 0·020N-acid, and after addition of methanol to another portion (to solvolyse any methyl perchlorate [27]) titration showed 0·18N total acid. Allowing for 0·02N-acid formation before methanolysis of methyl perchlorate, this corresponds to formation of 0·16M-methyl perchlorate (80% yield). Some difficulty resulted from a creeping and unstable endpoint, indicating that at least a part of the acid concentration may result from fairly slow methanolysis of a compound previously formed by interaction with nitromethane.

An orange-red amorphous solid remaining after evapor-

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[21] P. F. G. Praill, *J. Chem. Soc.*, 1957, 3162.

[22] H. Burton, D. A. Munday, and P. F. G. Praill, *J. Chem. Soc.*, 1956, 3933.

[23] H. Burton and G. W. H. Cheeseman, *J. Chem. Soc.*, 1953, 832.

[24] G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, 1964, **86**, 1039.

[25] For a brief review of the early chemistry of perchlorate esters, see N. V. Sidgwick, 'The Chemical Elements and Their Compounds,' Oxford University Press, London, 1950, pp. 1235—1236.

[26] J. Radell, J. W. Connolly, and A. J. Raymond, *J. Amer. Chem. Soc.*, 1961, **83**, 3958.

[27] J. Koskikallio, *Suomen Kem.*, 1967, **40B**, 131.

ation of the product solution decomposed on heating and gave an acid reaction in water. Repeated filtration of the dark red solution through molecular sieves reduced, but did not eliminate, both the intensity of the colour and the acidity. On being kept at room temperature the filtrate darkened and the acid concentration increased; the data are reported in Table 2. The rate of this acid development is, however, considerably less than the rate of formation of products from methyl iodide and silver perchlorate and only a negligible amount of the acid development during the kinetic runs could have resulted from covalent methyl perchlorate.

TABLE 2

Development of acid, as determined by titration against methanolic sodium methoxide, in a 0·15M solution of methyl perchlorate at 25·0° and calculated specific rate of reaction of the methyl perchlorate

t/min	0	1230	4140	6600	17100
[Acid]/N	0·008	0·011	0·016	0·022	0·040
10^7k_1/s^{-1}		(3·5)	2·4	2·6	2·0

RESULTS

(i) *Effect of Variation of Silver Perchlorate Concentration.*—With a constant initial concentration of methyl iodide (0·112M) a series of runs was carried out at 25·0°, the initial stoicheiometric silver perchlorate concentration being varied in the range 0·0008—0·22M. Both the overall extent of reaction as measured by consumption of silver ion and the percentage of this reaction proceeding with acid formation were monitored. The initial first-order rate coefficients with respect to silver perchlorate and the extent of acid formation are in Table 3.

TABLE 3

Initial first-order rate coefficients (k) with respect to silver perchlorate at varying concentrations with 0·112M-methyl iodide, and the percentage of overall reaction proceeding with acid formation in nitromethane at 25·0°

Initial [AgClO$_4$]/M	0·221	0·183	0·111	0·0736
10^5k/s^{-1}	16·6	13·8	12·0	6·7
Acid (%)	18	17	17	16
Initial [AgClO$_4$]/M	0·0553	0·0368	0·0276	0·0184
10^5k/s^{-1}	5·1	3·1	1·85	1·25
Acid (%)	20	15	15	15
Initial [AgClO$_4$]/M	0·0138	0·00919	0·00689	0·00459
10^5k/s^{-1}	1·09	0·96	0·93	0·83
Acid (%)	18	13	16	
Initial [AgClO$_4$]/M	0·00173	0·000867		
10^5k/s^{-1}	0·93	0·84		

At the higher silver perchlorate concentrations, the integrated first-order rate coefficients drifted downwards throughout each run, reached a minimum, and then increased. At intermediate (0·03—0·005M) concentrations, the values remained constant and the mean value was considered as equivalent to the initial value. At the lower silver perchlorate concentrations, the values drifted upwards throughout each run. The three runs presented in Table 1 illustrate each of the above types of behaviour. The simplest explanation of these observations is that, coupled with a fall-off due to the kinetic order actually being higher than unity, autocatalysis[28] occurs and tends to cause an increase as reaction proceeds. Since the order in silver perchlorate rises with increases in its concentration (slope of Figure 1), it is to be expected that the tendency for the experimental first-order rate coefficients to fall as reaction proceeds will be greater at the higher concentrations.

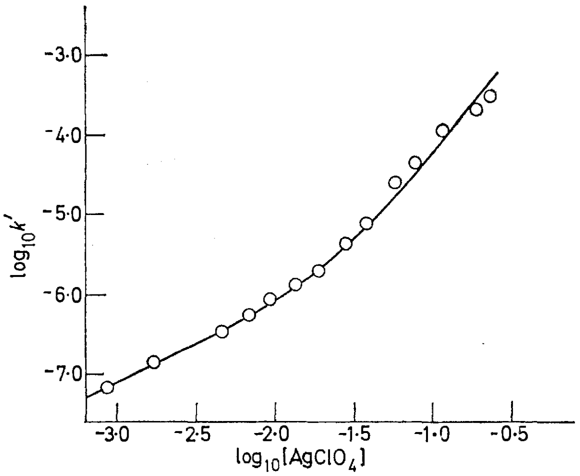

FIGURE 1 Logarithmic plot of initial first-order rate coefficient with respect to methyl iodide against the concentration of silver perchlorate in its reaction with 0·112M-CH$_3$I in CH$_3$NO$_2$ at 25°

A logarithmic plot of the initial first-order rate coefficients with respect to methyl iodide ($k' = k$[AgClO$_4$]/[CH$_3$I]) against the initial concentration of silver perchlorate is presented in Figure 1. The slope at any point gives the experimental order in silver perchlorate for that concentration.

(ii) *Effect of Variation of Methyl Iodide Concentration.*—For a constant initial concentration of silver perchlorate (0·0342M), a series of runs was carried out at 25·0° with initial methyl iodide concentration in the range 0·01—0·44M. Both the overall extent of reaction, as measured by consumption of silver ion, and the percentage of this reaction proceeding with acid formation were monitored. The initial first-order rate coefficients with respect to silver perchlorate and the extent of acid formation are reported in Table 4.

TABLE 4

First-order rate coefficients (k) with respect to 0·0342M-silver perchlorate with varying initial concentrations of methyl iodide and the percentage of overall reaction proceeding with acid formation, in nitromethane at 25·0°

[CH$_3$I]/M	10^5k/s^{-1}	Acid (%)
0·440	4·8	25
0·331	4·1	22
0·223	3·5	19
0·162	3·1	18
0·112	2·7	16
0·0558	1·57	19
0·0279	0·85	22
0·0134	0·50	17

The initial silver perchlorate concentration chosen for the study was such that the integrated first-order rate coefficients

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[28] P. S. Walton and M. Spiro, *J. Chem. Soc.* (*B*), 1969, 42.

remained essentially constant throughout the extent of reaction which was followed and mean values are reported.

An unusual feature of these experiements is the less than linear increase in the value of the first-order rate coefficient with increase in methyl iodide concentration; this is illustrated in Figure 2. The vast majority of reactions with a fixed initial concentration of inorganic reagent show a linear relationship between initial rate (which is proportional to the plotted first-order rate coefficient) and initial organic substrate concentration.

(iii) *Effect of Added Tetraethylammonium Perchlorate.*—With fixed initial concentrations of 0·0367M-silver perchlorate and 0·112M-methyl iodide, a series of runs was carried out at 25·0° with varying concentrations of added tetraethylammonium perchlorate. Only relatively modest rate increases were observed with increases in concentration of the additive. Both overall extent of reaction and acid formation were monitored, as outlined previously. Average first-order rate coefficients with respect to silver perchlorate (equated to initial values due to the previously discussed fortuitous absence of drift) and values for the percentage of reaction proceeding with acid formation are reported in Table 5.

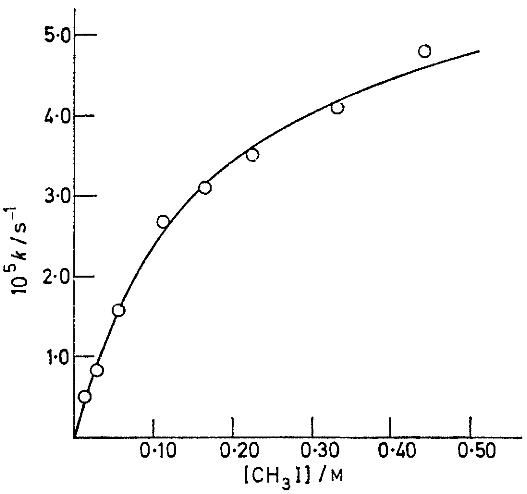

FIGURE 2 Plot of the initial first-order rate coefficient with respect to 0·0342M-$AgClO_4$ against the stoicheiometric concentration of CH_3I for reactions in CH_3NO_2 at 25°

TABLE 5

Initial first-order rate coefficients (k) with respect to 0·0368M-silver perchlorate in its reaction with 0·112M-methyl iodide in the presence of varying concentrations of tetraethylammonium perchlorate, and the percentage of reaction proceeding with acid formation, in nitromethane at 25·0°

$[NEt_4ClO_4]$/M	0·0000	0·0184	0·0367	0·073
$10^5k/s^{-1}$	3·1 [a]	3·4	3·7	4·2
Acid (%)	15 [a]	16	15	17
$[NEt_4ClO_4]$/M	0·111	0·165	0·219	
$10^5k/s^{-1}$	4·8	5·6	5·8	
Acid (%)	17	15	17	

[a] From Table 3.

DISCUSSION

A significant observation is the less than linear increase in initial rate with increasing initial concentration of methyl iodide for a constant initial concentration of silver perchlorate. This behaviour parallels the Michaelis–Menton kinetics frequently observed in enzyme studies,[29] and the pre-equilibrium association (1) of methyl iodide

$$CH_3I + Ag^+ \overset{K}{\rightleftharpoons} (CH_3IAg)^+ \qquad (1)$$

(equivalent to substrate) and silver ion (equivalent to enzyme), prior to the rate-determining step, is suggested. Such behaviour can be analysed in terms of two parameters, an association constant K for formation of the complex and a rate coefficient $k^{(\mathrm{MeI}\rightarrow\infty)}$ for its subsequent reaction. By using the limiting rate coefficient at high methyl iodide concentration (obtained, as indicated in Table 6, by extrapolation of experimental values) and a best-fit value for the association constant (so as to minimize deviation of calculated from experimental rate coefficients), it is found that initial first-order rate coefficients can be calculated which are in excellent agreement with those experimentally determined (Table 6). This can be taken as strong experimental evidence that this reaction (and probably other silver-ion assisted reactions of alkyl halides) involves the pre-equilibrium formation and subsequent reaction of an alkyl halide-silver ion complex.[8-11] Brief studies of the reaction in nitrobenzene,[1] rather than nitromethane, and of the reaction of neopentyl iodide with silver perchlorate in nitromethane[30] have also been successfully analysed in this way.

TABLE 6

Comparison of initial experimental (k^e) and calculated [a] (k^c) first-order rate coefficients with respect to 0·0342M-silver perchlorate with varying concentrations of methyl iodide at 25.0°

$[CH_3I]$/M	0·440	0·331	0·223	0·162
$10^5k^e/s^{-1}$	4·8	4·1	3·5	3·1
$10^5k^c/s^{-1}$	4·4	4·1	3·5	3·1
$[CH_3I]$/M	0·112	0·0558	0·0279	0·0134
$10^5k^e/s^{-1}$	2·7	1·57	0·85	0·50
$10^5k^c/s^{-1}$	2·7	1·55	0·88	0·45

[a] Calculated from $k^c = k^{(\mathrm{MeI}\rightarrow\infty)}[CH_3IAg^+]/[AgClO_4]$, where $k^{(\mathrm{MeI}\rightarrow\infty)}$ is the limiting first-order rate coefficient at high methyl iodide concentrations ($5\cdot7 \times 10^{-5}$ s^{-1}), obtained by extrapolation of a plot of k^{e-1} against $[CH_3I]^{-1}$ to zero $[CH_3I]^{-1}$, and $[CH_3IAg^+]$ is calculated by using a best-fit value for the association constant K(8·1 l mol^{-1}).

Reactions in acetonitrile,[4,6,8,11] while frequently showing complex kinetic orders with respect to the silver salt, have always, within the concentration ranges studied, been first order with respect to the alkyl halide. This observation, coupled with the much slower rates of reaction relative to those in benzene,[8d,14] nitrobenzene,[1] or nitromethane[30] suggests that the relatively strong solvation of the silver ion in acetonitrile leads to only a

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[29] See, for example, C. Walter, ' Steady-state Applications in Enzyme Kinetics,' Roland Press, New York, 1965, pp. 24—36.

[30] D. N. Kevill, G. H. Johnson, and V. V. Likhite, *Chem. and Ind.*, 1969, 1555.

small equilibrium concentration of alkyl halide–silver ion complex being formed within this solvent.

For a constant initial concentration of methyl iodide, the effect of variation of the initial silver perchlorate concentration (Figure 1) is rather complex. At low concentrations, the kinetic order with respect to silver perchlorate approaches unity but the order increases with increase in concentration, reaching a value of *ca.* 2·7 at 0·22M-silver perchlorate. Similar behaviour has previously been observed for the reaction of silver perchlorate with 2-bromo-octane in acetonitrile.[8b] Additions of tetraethylammonium perchlorate, into a constant initial concentration of silver perchlorate, cause relatively modest increases in the first-order rate coefficient with respect to stoicheiometric silver ion (Table 5) and, therefore, the increase in order with increasing silver perchlorate concentrations does not appear to be primarily due either to a general type of salt effect or to the incursion of pathways involving nucleophilic assistance by perchlorate ion within the rate-determining step. Possible explanations include long-range influences of additional silver ions upon the reaction pathway, specific interaction of more than one silver ion,[31] or a situation where the ability to transfer a silver ion to the methyl iodide deviates considerably from a linear relationship with concentration at the higher silver perchlorate concentrations. The latter may well be the better rationalization, reminiscent of those acid-catalysed reactions of bases whose rates are correlated with the h_0 function rather than stoicheiometric acid concentration;[32] possibly, if a sufficiently large number of systems were studied, related 'electrophilicity functions' could be set up for silver-ion assisted reactions.

In view of the reported inertness of alkyl perchlorates towards nitromethane,[22,23] it was somewhat surprising to find that *ca.* 20% of the reaction proceeded to form not methyl perchlorate but an uncharacterized red amorphous solid. However, once formed, methyl perchlorate reacts too slowly with nitromethane (Table 2) to account for the observed acid and, therefore, the reaction leading to acid development must be occurring concurrently with, and not subsequent to, methyl perchlorate formation.

The percentage of reaction proceeding with acid formation remained essentially constant throughout each run (Table 1) and it was independent of the initial concentrations of silver perchlorate (Table 3), methyl iodide (Table 4), and added tetraethylammonium perchlorate (Table 5). For acid formation concurrent with perchlorate ester formation, this places severe restrictions upon the possible mechanism. Similar observations have been made previously[3,6,8,33] and have been rationalized in terms of product formation *via* an ion pair containing the anion of the silver salt and the carbonium ion. Since the product ratio has been found to vary with change in identity of the halogen in the alkyl halide, it has been suggested[8,33] that the product partitioning is largely determined while the ion-pair is part of a halide ion containing aggregate.

The mechanism is formulated[8] in Scheme 1. However, the driving force for bimolecular attack of a nucleophile upon a covalently bonded substrate is generally considered to be the formation of the new bond concurrent with the breaking of the old one and this does not occur in step (3). Scheme 1 should possibly be expanded to include formation of an entity approaching an ion-triplet, which usually reverts to alkyl halide-complexed silver ion but which can also be stabilized by association with the anion of the added silver salt to give a quadrupole (Scheme 2). Either step (3a or b) could be rate determining and this mechanism parallels one proposed[34] for one type of merged substitution and elimination reaction of tertiary structures, in which the carbon–halogen bond is fairly easily heterolysed even in the absence of electrophilic assistance. Sneen and his co-workers[35,36] subsequently presented evidence for a mechanism of this type for several nucleophilic substitution reactions of secondary substrates; the validity of their interpretation of the experimental data has, however, been questioned.[37] Their mechanism was originally formulated in terms of discrete ionic species and it did not include either ion-pairs immediately preceding product formation or the probable intermediacy of an ion-triplet.[38-40] Recently, Sneen has recognized both the need for amplification of the original mechanism and the probability of some covalent character within the various interme-

$$\mathrm{RX} + \mathrm{Ag}^+ \rightleftharpoons (\mathrm{RX}\cdots\mathrm{Ag})^+ \qquad (2)$$

$$\mathrm{Y}^- + \mathrm{RX}\cdots\mathrm{Ag}^+ \overset{\text{r.d.}}{\rightleftharpoons} \mathrm{Y}^-\mathrm{R}^+\mathrm{X}^-\mathrm{Ag}^+ \qquad (3)$$

$$\mathrm{Y}^-\,\mathrm{R}^+\mathrm{X}^-\mathrm{Ag}^+ \xrightarrow[\text{several steps}]{\text{fast}} \text{Products} \qquad (4)$$

SCHEME 1

$$\mathrm{RX} + \mathrm{Ag}^+ \rightleftharpoons (\mathrm{RX}\cdots\mathrm{Ag})^+ \qquad (2)$$

$$\mathrm{RX}\cdots\mathrm{Ag}^+ \rightleftharpoons (\mathrm{R}\cdots\mathrm{X}\cdots\mathrm{Ag})^+ \qquad (3a)$$

$$\mathrm{Y}^- + (\mathrm{R}\cdots\mathrm{X}\cdots\mathrm{Ag})^+ \rightleftharpoons \mathrm{Y}^-\mathrm{R}^+\mathrm{X}^-\mathrm{Ag}^+ \qquad (3b)$$

$$\mathrm{Y}^-\mathrm{R}^+\mathrm{X}^-\mathrm{Ag}^+ \xrightarrow{\text{fast}} \text{Products} \qquad (4)$$

SCHEME 2

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[31] E. S. Rudakov, V. V. Zamashchikov, and R. I. Rudakova, *Org. Reactivity* (*English Edn.*), 1970, **7**, 363.

[32] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

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

[34] D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 1961, 252; *J. Amer. Chem. Soc.*, 1961, **83**, 3815.

[35] H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, 1965, **87**, 287, 292.

[36] R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 1969, **91**, 362, 6031.

[37] See, for example, D. J. McLennan, *J.C.S. Perkin II*, 1974, 481.

[38] D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1966, **88**, 4469.

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[40] J. Koskikallio, *Acta Chem. Scand.*, 1972, **26**, 1201.

diates.[41] For substitution the amplified and revised mechanism is given in Scheme 3; this now becomes identical with one branch of the previously proposed mechanism of merged substitution and elimination (Scheme 4).[34]

$$\begin{aligned}
&\mathrm{RX} \rightleftharpoons \mathrm{R}^{\delta+}\cdots\mathrm{X}^{\delta-}\\
&\mathrm{Y}^{-} + \mathrm{R}^{\delta+}\cdots\mathrm{X}^{\delta-} \longrightarrow \mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta\delta+}\cdots\mathrm{X}^{\delta-}\\
&\mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta\delta+}\cdots\mathrm{X}^{\delta-} \rightleftharpoons \mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta+} + \mathrm{X}^{-}\\
&\mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta+} \rightleftharpoons \mathrm{YR}
\end{aligned}$$

SCHEME 3

$$\mathrm{RX} \rightleftharpoons \mathrm{R}^{\delta+}\cdots\mathrm{X}^{\delta-}$$

$$\mathrm{Y}^{-} + \mathrm{R}^{\delta+}\cdots\mathrm{X}^{\delta-} \rightleftharpoons \mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta\delta+}\cdots\mathrm{X}^{\delta-}$$

$$\begin{tikzcd}
 & \mathrm{Y-R} + \mathrm{X}^{-} \\
\mathrm{Y}^{\delta-}\cdots\mathrm{R}^{\delta\delta+}\cdots\mathrm{X}^{\delta-} \arrow[ur] \arrow[dr] & \\
 & \text{Alkene} + \mathrm{HY} + \mathrm{X}^{-}
\end{tikzcd}$$

SCHEME 4

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