

The Electrophilic Nature of Triarylmethyl Substrates in Acetonitrile

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Through competition experiments between various inorganic pseudohalide ions, the electrophilic nature of some substituted and unsubstituted triphenylmethyl halides and perchlorates in an aprotic solvent, acetonitrile, has been examined. For all substrates examined, the reactivity sequence has been found to be $N_3^- \sim NC^- \sim OCN^- > SCN^-$, suggesting that the so-called azide probe is of limited usefulness toward this class of substrates in acetonitrile.

In the presence of an ionic perchlorate the relative reactivity of the azide ion is increased while the presence of nucleophilic anions levels the reactivities of the applied pseudohalide ions. It is suggested that nucleophilic anions are able to deionize the carbenium ions or separated ion pairs to species of lower charge separation. Since this deionization has been found to be extremely rapid, the reacting species from the triarylmethyl substrates are approximately the same, regardless of whether highly ionized triarylmethyl perchlorates or very weakly dissociated triarylmethyl halides are employed as reactants. The rather similar relative reactivities of the various pseudohalide ions toward triarylmethyl halides and triarylmethyl perchlorates substantiate this conclusion.

Finally, the consequences of the deionization mechanism on salt effects are discussed. It is concluded that the deionization mechanism is the probable cause for the very negative salt effects observed in certain S_N1 reactions. The deionization mechanism appears to be limited to reactions of substrates which give highly delocalized carbenium ions.

The fundamental studies by Winstein and co-workers¹ have resulted in the general acceptance of the fact that the S_N1 mechanism of saturated carbon compounds, RX , is highly complex. A number of species may be the reacting one, depending upon the substrate, the nucleophile, the solvent, the ionic strength *etc.* Several species like those depicted in the Winstein dissociation scheme,² in addition to

various types of solvent-separated ion-pairs,³⁻⁵ may well give rise to first order kinetics and a racemic product. Since the electrophilic nature of the reacting carbon atom undoubtedly varies greatly with the stretching of the $R-X$ bond, various reactivity sequences may be observed and yet the usual characteristics of an S_N1 mechanism may still apply.

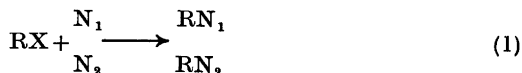
The majority of the reactions of saturated carbon compounds which satisfy the criteria of being S_N1 reactions are solvolysis reactions in protic or mixed solvents. These reactions, however, appear to constitute a special class of S_N1 reactions, probably due to the ability of protic solvents to hydrogen bond to most of the usual leaving groups and thus favour the formation of ionic species. For reactions performed in protic solvents, positive salt effects are in most cases observed,^{2,6,7} regardless of whether the increased ionic strength is due to salts of nucleophilic or non-nucleophilic anions, contrary to what is found for reactions performed in dipolar aprotic solvents.⁸⁻¹⁰ The exceptional salt effects on S_N1 reactions observed in dipolar aprotic solvents suggest that further knowledge of S_N1 -type reactions in aprotic solvents may shed some light upon S_N1 reactions in general. Parker,¹¹ particularly, has stressed the importance of studying S_N2 reactions in dipolar aprotic solvents, primarily to avoid the effect of solvation of the reacting nucleophile. In the case of studies on substrates exhibiting S_N1 behaviour it appears even more important to do so, due to the additional effect of protic species upon the substrate.

Unfortunately, when examining reactions of substrates reacting by the S_N1 mechanism in dipolar aprotic solvents, there are several experimental difficulties which are not readily

oped with. This is primarily caused by the fact that since the most usual S_N1 reactions are alcoholysis and similar solvolysis reactions which necessarily can not be studied, the actual number of possible reactions available for detailed study is greatly diminished. Furthermore, accurate kinetic studies on S_N1 reactions in dipolar aprotic solvents are in most cases difficult to perform due to the high rates of these reactions, requiring the use of special techniques.^{12,13} Several attempts were made during the present study to measure the rates of the reaction between unsubstituted triphenylmethyl halides and perchlorate and various inorganic anions in acetonitrile: the stopped-flow technique was utilised as described in the Experimental Part. The rates of the reactions, however, could not be determined, confirming the previous findings of extremely high rates of reaction.^{12,13} The only kinetic study on reactions between carbenium ions⁵ and various nucleophiles in dipolar aprotic solvents has been performed on stabilized dyestuff cations,¹³ where the high rates of reaction prevented a detailed investigation.

Apart from some isomerizations,¹⁰⁻¹⁴ few reactions are therefore available for studies on S_N1 reactions in aprotic solvents. This leaves the classical competition experiments,^{9,15} employing S_N1 -type substrates as a natural mode of attacking the problem of obtaining further information on S_N1 reactions in dipolar aprotic solvents. In this work we want to report the results of experiments of this type performed in acetonitrile employing some triarylmethyl com-

pounds as substrates and applying various pseudohalide ions as nucleophiles, eqn. 1.



R = Ph₃C, X = Cl, Br and ClO₄.
R = (4-MePh)₃C and (4-MeOPh)₃C, X = Cl
N = N₃⁻, NC⁻, OCN⁻, and SCN⁻.

The triarylmethyl compounds and the pseudohalide ions are well suited for this type of experiment since, in most cases, both the products and the unreacted pseudohalide ions can be rapidly determined with high accuracy applying solution IR. In Table 1 are listed the absorption frequencies and integrated extinction coefficients in the 2000–2300 cm⁻¹ region of the triphenylmethyl pseudohalides and the pseudohalide ions measured in acetonitrile. (For the sake of brevity, only the constants for unsubstituted triphenylmethyl compounds are listed in Table 1).

In none of the examined reactions could products resulting from *para*-attack, *p*-benzhydrylphenyl pseudohalides (I), be detected. Only the normal products, triphenylmethyl pseudohalides (II) could be isolated. Due to the small steric demands of the applied nucleophiles, products like (I) are not to be expected.¹³

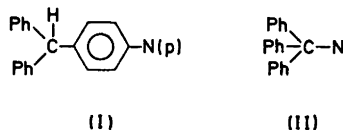


Table 1. Absorption frequencies in the 2000–2300 cm⁻¹ range of triphenylmethyl pseudohalides and pseudohalide ions in acetonitrile together with half-band widths and integrated extinction coefficients at 25 °C.

X ⁻	Ph ₃ CX	ν cm ⁻¹	$\nu_{\frac{1}{2}}$ cm ⁻¹	$A \times 10^{-4} M^{-1} cm^{-2}$
CN ^{-a}	Ph ₃ CCN ^b	2058	14	0.059
	Ph ₃ CNC ^b	2239	8	0.055
	Ph ₃ CNC ^b	2126	11	1.0
N ₃ ^{-a}	Ph ₃ CN ₃ ^c	2005	10	7.2
	Ph ₃ CN ₃ ^c	2102	10	1.4
OCN ^{-a}	Ph ₃ CNCO ^d	2140	23	5.2
	Ph ₃ CNCO ^d	2252	12	9.1
SCN ^{-a}	Ph ₃ CNCS ^d	2059	12	4.1
	Ph ₃ CNCS ^d	2047	100	15

^a Ref. 16. ^b Ref. 17 (measurements performed in carbon tetrachloride). ^c Ref. 10. ^d This work.

The use of the triarylmethyl compounds as substrates offered an additional advantage due to the fact that these compounds range from very weakly dissociated compounds $X = \text{Cl}$ and Br , to extensively dissociated ones, $X = \text{ClO}_4$ (see Experimental Part). Furthermore, as none of the usual inorganic anions, Cl^- , Br^- , ClO_4^- , etc., absorb in the 2000–2300 cm^{-1} region, the measurements according to eqn. 1 could be performed at greatly varying ionic strength by addition of the appropriate salts.

Acetonitrile was chosen as solvent, as its low donicity keeps to a minimum the effects of possible reaction between substrate and solvent.¹⁹ Tetraphenylarsonium salts were in all cases used as the source of the nucleophilic anions to ensure a complete dissociation in acetonitrile.

EXPERIMENTAL

Materials. The purification of acetonitrile and the applied tetraphenylarsonium salts was performed as previously reported.¹⁶ Dichloromethane, "Baker Analyzed" reagent, was distilled from phosphorus pentoxide and finally from calcium hydride prior to use. Lithium perchlorate, Fluka *purum* wasserfrei, was used without further purification.

Triphenylmethyl chloride and triphenylmethyl bromide, both Fluka *purum*, were purified as reported.¹⁷ Triphenylmethyl perchlorate was made according to Longworth and Mason.²⁰ M.p. 148–149 °C, (150 °C²⁰).

4,4',4''-Trimethyltriphenylmethyl chloride was prepared from the corresponding alcohol and crystallized several times from acetonitrile. M.p. 176–178 °C, (180 °C²¹).

4,4',4''-Trimethoxytriphenylmethyl chloride, EGA-Chemie KG, was repeatedly crystallized from dry acetonitrile.

Stock solutions of the substrates and the various anhydrous tetraphenylarsonium salts were made prior to use according to a previously described procedure.¹⁷

The melting points are corrected.

Competition experiments. Assuming the nucleophiles to react with the same species forming the products in first order reactions with respect to the attacking nucleophiles, the relative rates are given by:

$$\frac{k_{N_1}}{k_{N_2}} = \frac{[\text{RN}_1]/[\text{N}_1]}{[\text{RN}_2]/[\text{N}_2]} \quad (2)$$

where $[\text{RN}_1]$ and $[\text{RN}_2]$ are the concentrations of the products, respectively, and $[\text{N}_1]$ and $[\text{N}_2]$ are the initial concentrations of the reacting nucleophiles. As the k_{N_1}/k_{N_2} ratios for the ma-

jority of the competition reactions examined were found to be close to unity, equal concentrations of the nucleophiles were applied and eqn. 2 reduces to eqn. 3:

$$k_{N_1}/k_{N_2} = [\text{RN}_1]/[\text{RN}_2] \quad (3)$$

Due to the unstable nature of the triarylmethyl isoselenocyanates in acetonitrile, particularly in the presence of cyanide ions,²² reactions with the selenocyanate ion were not included in this study. In the other reactions studied, the products were found to be stable in the presence of unreacted reactants, at least at our time-scale. (The product composition did not change as judged by the IR spectrum of the reaction mixture immediately after mixing, and after a delay of 15 to 20 minutes). However two exceptions were noted: 4,4',4''-trimethyltriphenylmethyl isothiocyanate was found to react rather rapidly with ionic cyanide and cyanate causing low accuracy in the $k_{\text{CN}^-}/k_{\text{SCN}^-}$ and $k_{\text{OCN}^-}/k_{\text{SCN}^-}$ ratios when 4,4',4''-trimethyltriphenylmethyl chloride was the substrate. The isothiocyanate from 4,4',4''-trimethoxytriphenylmethyl chloride was so unstable in the presence of the other ions that the thiocyanate ion could not be included in the competition experiments toward this substrate. The unstable nature of triarylmethyl isothiocyanates has previously been noted.²³

When the cyanide ion was one of the reacting ions, the yield of triarylmethyl cyanide and the amount of unreacted ionic cyanide were calculated from the peak heights due to the competing anion and the product formed from this anion. This procedure was necessary because of the low extinction coefficients of ionic cyanide and of the triarylmethyl cyanides. No attempt was made to determine the relative amounts of triarylmethyl cyanide and of triarylmethyl isocyanide when cyanide ion was employed as reagent. Concentration of reagents at least one order of magnitude higher than generally applied in this study, $\approx 1 \times 10^{-3}$ M, would have been necessary to obtain reliable information about the ambident nature of the cyanide ion toward the various substrates.¹⁷

When the thiocyanate ion was one of the reactants, the amount of the organic isothiocyanate formed was not usually estimated due to the broadness of this absorption in the 2050 cm^{-1} region (see Table 1).

The general procedure was to add a 1:1 mixture of the nucleophiles to the freshly prepared solution of the triarylmethyl substrate. Each of the nucleophiles was slightly in excess, 3 to 5 %, of the reacting substrate. In the case of the triarylmethyl halides, the product composition was found to be independent of whether the nucleophiles were added to the substrate or *vice versa*. Likewise, the rate of mixing did not appear to cause a significant change in the product composition. When triphenylmethyl perchlorate was the substrate, however, the relative

yields of products appeared to be highly dependent upon how the solutions were mixed.

The results from the competition experiments are listed in Tables 2 to 4. In Tables 5 to 7 are listed the results of competition experiments with 4,4',4''-trimethoxytriphenylmethyl chloride as substrate, performed in the presence of various amounts of lithium perchlorate, tetraphenylarsonium perchlorate and tetraphenylarsonium chloride, respectively.

The competition ratios were calculated from experiments performed at least in duplicate. The differences between parallel determinations were within the experimental error due to the uncertainties in the peak heights. Only in the case where triphenylmethyl perchlorate was the substrate did the discrepancy between the parallel determinations exceed the calculated maximum uncertainty. In the competition experiments where both the products could be determined, the total yield of products was found to be quantitative as calculated from the amount of the reacting substrate.

The IR measurements were performed with a Unicam SP 200 G Infrared Spectrophotometer at 25 ± 1 °C applying 0.1 cm liquid cells.

Dissociation constants of triphenylmethyl compounds in acetonitrile at 25.0 °C. A: Triphenylmethyl perchlorate. A solution of triphenylmethyl perchlorate in dichloromethane showed two peaks of similar intensity in the 400–500 nm region. The molar extinction coefficients at 25 °C of the peaks at 434 nm and 410 nm were $3.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $3.68 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, in excellent agreement with published values.^{20,24}

In acetonitrile the two peaks were shifted to 430 and 403 nm and the molar extinction coefficients of these peaks ranged from 3.5×10^4 to $3.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and were found to be independent of the concentration of triphenylmethyl perchlorate in the $5 - 20 \times 10^{-4} \text{ M}$ region, suggesting this compound to be completely dissociated in acetonitrile in this concentration range. The experimentally determined value for the extinction coefficient in acetonitrile is lower than the value reported in the literature, $4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.^{25,26} For lower concentrations of triphenylmethyl perchlorate than $3 \times 10^{-4} \text{ M}$, a slight but significant reduction of the molar extinction coefficient in acetonitrile was observed. As the observed molar extinction coefficients in dichloromethane were in agreement with the published values, it appears safe to conclude that the lower extinction coefficients observed in acetonitrile on extreme dilution were due to some impurity in the applied solvent, most probably traces of water, and not to impurities in the applied samples of triphenylmethyl perchlorate.

Conductance measurements of freshly prepared solutions of triphenylmethyl perchlorate in acetonitrile at 25.0 °C were performed and the $\Lambda - c^{1/2}$ plots were found to be, within the experimental error, completely linear for con-

centrations in the $2.5 - 7 \times 10^{-4} \text{ M}$ range. (On further lowering of the concentration a significant increase in the equivalent conductivity was observed. A deviation from linearity in the $\Lambda - c^{1/2}$ plot at low concentrations is to be expected if traces of water are present in the solvent). On extrapolation to infinite dilution, a limiting equivalent conductivity of $166.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for triphenylmethyl perchlorate was calculated.

Conductance measurements on tetraphenylarsonium perchlorate in acetonitrile at 25.0 °C gave conductance parameters for this salt in excellent agreement with those determined by Springer and co-workers.²⁷ The nearly identical slopes in the $\Lambda - c^{1/2}$ plots for the two examined compounds can be considered as additional evidence for the complete dissociation of triphenylmethyl perchlorate in acetonitrile. From the limiting equivalent conductivity of $166.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for triphenylmethyl perchlorate and the literature value for $\lambda_0(\text{ClO}_4)$,²⁷ the limiting equivalent conductivity of the triphenylmethyl carbenium ion, $\lambda_0(\text{Ph}_3\text{C}^+)$, was calculated to be $62.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in acetonitrile at 25.0 °C.

B. Triphenylmethyl chloride and triphenylmethyl bromide. From UV measurements of 0.02 M solutions of triphenylmethyl chloride and triphenylmethyl bromide, the dissociation constants for these two compounds in acetonitrile at 25.0 °C were found to be 7.0×10^{-11} and $9.6 \times 10^{-10} \text{ M}$, respectively. Calculations based upon conductance measurements in acetonitrile, and applying the calculated limiting equivalent conductivity for the triphenylmethyl carbenium ion and values in the literature for $\lambda_0(\text{Cl}^-)$ ²⁸ and $\lambda_0(\text{Br}^-)$,²⁷ gave dissociation constants for these two substrates in acetonitrile which were generally ten times those determined by the UV method. Since traces of water in the applied solvent will give too low values by the UV method and too high values by the conductance method for the dissociation constants, the observed discrepancy between the two set of measurements is to be expected. The exact values of the dissociation constants of triphenylmethyl chloride and triphenylmethyl bromide are of limited importance to the discussion of the results from the competition experiments.

C. Dissociation of triphenylmethyl substrates in the presence of salts of inorganic anions. Attempted Stopped-Flow measurements. On adding small amounts of various salts of nucleophilic anions to triphenylmethyl perchlorate dissolved in acetonitrile, the colour of the solutions disappeared instantaneously. The reactions between a $5 \times 10^{-5} \text{ M}$ solution of triphenylmethyl perchlorate and $1 \times 10^{-3} \text{ M}$ solutions of tetraphenylarsonium azide, tetraphenylarsonium bromide, and tetraphenylarsonium iodide, respectively, were studied by a Stopped-Flow Spectrophotometer. The rates of the reactions, however, were extremely rapid and could not be determined by this technique. Assuming

the reactions to be second order, a lower limit of the rate constants of $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ could be estimated from these measurements.

On adding tetraphenylarsonium perchlorate to a solution of triphenylmethyl bromide a small but significant increase of the colour of the solution due to the triphenylmethyl carbenium ion was observed. (In a saturated solution of tetraphenylarsonium perchlorate in acetonitrile, $1.5 \times 10^{-2} \text{ M}$, the concentration of the triphenylmethyl carbenium ion from a $1 \times 10^{-2} \text{ M}$ solution of triphenylmethyl bromide was twice that when this substrate was dissolved in pure acetonitrile). The rate of the increase of the concentration of the triphenylmethyl carbenium ion from triphenylmethyl bromide in acetonitrile upon the addition of various amounts of tetraphenylarsonium perchlorate was extremely high and could not be determined by the stopped-flow technique.

Conductance measurements confirmed the trend in the results from the UV measurements. The conductivity of a solution, $1.005 \times 10^{-2} \text{ M}$ in triphenylmethyl bromide and $6.08 \times 10^{-4} \text{ M}$ in tetraphenylarsonium perchlorate, was 3.5 % higher than the calculated conductivity if no increase in the ionization had taken place. Similarly, the conductivity of a solution, $1.005 \times 10^{-2} \text{ M}$ in triphenylmethyl bromide and $6.18 \times 10^{-4} \text{ M}$ in tetraphenylarsonium iodide, was found to be 4.4 % lower than the calculated conductivity if no decrease in the ionization had taken place.

Conductance measurements. The measurements were performed with a Conductivity Meter CDM3 employing an immersion type conductivity cell, CDC 403, with a cell constant of 1.00 cm. The conductivity of the applied acetonitrile was less than $1 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$.

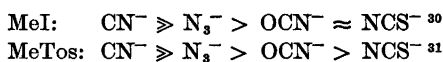
Stopped-flow measurements. The measurements were performed with a Durrum Stopped-Flow Model D-110.

RESULTS

In Table 2 are listed the $k_{\text{N}_3^-}/k_{\text{CN}^-}$ ratios for the various triarylmethyl substrates at 25 °C in

acetonitrile. (The results in Table 2 and in the following tables refer to experiments in which the mixture of the competing nucleophiles was added to the substrate if not otherwise stated).

The results in Table 2 clearly show that the azide ion, being an α -nucleophile, and an often used trapping agent for carbenium ions in solvolysis reactions,²⁹ is only as reactive as are the cyanate ion and the cyanide ion as viewed from the experimentally determined competition ratios, $k_{\text{N}_3^-}/k_{\text{OCN}^-}$ and $k_{\text{N}_3^-}/k_{\text{CN}^-}$, respectively. This suggests that the azide probe is of limited reliability in reactions toward triarylmethyl substrates in acetonitrile, as noted by Darwish and Preston.¹⁵ From Table 2 it can also be seen that the effect of the *para*-substituents in triarylmethyl chlorides is small. Only toward triarylmethyl substrates containing substituents which strongly stabilize the carbenium ion, *i.e.* *p*-dialkylamino substituted derivatives, does the azide ion retain its exceptional reactivity in dipolar aprotic solvents.¹³ In the usual $\text{S}_{\text{N}}2$ reactions toward aliphatic carbon compounds in acetonitrile the azide ion does not behave exceptionally and the following reactivity sequences are known:

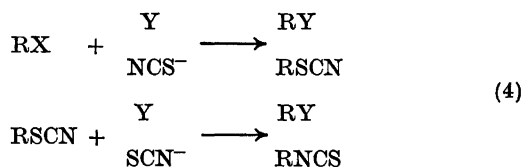


The thiocyanate ion appears to be significantly less reactive than the other three ions, as viewed from the competition experiments, and the relative reactivity of this ion toward the triarylmethyl substrates appears to parallel its reactivity in the typical $\text{S}_{\text{N}}2$ reactions. However, the thiocyanate ion may well act as a thionucleophile toward the triarylmethyl substrates and thus form an unstable triarylmethyl

Table 2. $k_{\text{N}_3^-}/k_{\text{CN}^-}$ ratios for various triarylmethyl substrates at 25 °C in acetonitrile.

Substrate	Substrate $\times 10^3 \text{ M}$	$k_{\text{N}_3^-}/k_{\text{CN}^-}$	$k_{\text{N}_3^-}/k_{\text{OCN}^-}$	$k_{\text{OCN}^-}/k_{\text{CN}^-}$
Ph_3CCl	1.33	2.17 ± 0.06	1.34 ± 0.06	1.52 ± 0.06
Ph_3CBr	1.33	1.81 ± 0.09	1.25 ± 0.09	1.25 ± 0.06
Ph_3CClO_4	1.34	1.54 ± 0.09	1.98 ± 0.1	0.90 ± 0.06
$(p\text{-MePh})_3\text{CCl}$	1.15	1.57 ± 0.09	1.75 ± 0.09	0.85 ± 0.05
$(p\text{-MeOPh})_3\text{CCl}$	1.19	1.41 ± 0.08	1.87 ± 0.1	0.71 ± 0.04
		$k_{\text{CN}^-}/k_{\text{SCN}^-}$	$k_{\text{OCN}^-}/k_{\text{SCN}^-}$	
Ph_3CCl	1.33	6.75 ± 0.1	10.5 ± 0.1	
Ph_3CBr	1.33	4.91 ± 0.06	6.35 ± 0.06	
$(p\text{-MePh})_3\text{CCl}$	1.15	$\leq 19 \pm 8$	$\leq 16 \pm 7$	

thiocyanate.³² During the isomerization of the first formed organic thiocyanate to the corresponding isothiocyanate, the ion competing with the thiocyanate ion for the original triaryl-methyl substrate, is allowed once more to compete for the triarylmethyl moiety, eqn. 4.



The results from the studies involving the thiocyanate ion may therefore be ambiguous.

The leaving group appears to exert a pronounced influence upon the various competition ratios. Increasing dissociation of the triaryl-methyl substrates seems to decrease the relative reactivity of the azide ion, and to increase the relative reactivity of the thiocyanate ion, but the general trend is by no means certain. The effect of the leaving group, however, is for most of the competition ratios significant, and should

Table 3. The effect of concentration of reactants upon $k_{\text{OCN}^-}/k_{\text{CN}^-}$ and $k_{\text{N}_3^-}/k_{\text{CN}^-}$.

Substrate	Substrate $\times 10^3$ M	$k_{\text{OCN}^-}/k_{\text{CN}^-}$
Ph ₃ CCl	1.35	1.52 ± 0.06
	13.3	1.56 ± 0.06
Ph ₃ CBr	1.35	1.25 ± 0.06
	13.3	1.35 ± 0.06
		$k_{\text{N}_3^-}/k_{\text{CN}^-}$
Ph ₃ CCl	1.35	2.17 ± 0.06
	4.0	2.14 ± 0.06
Ph ₃ CClO ₄	1.35	1.54 ± 0.09
	4.0	0.32 ± 0.02

Table 4. $k_{\text{N}_3^-}/k_{\text{CN}^-}$ as a function of mixing.

Substrate		Substrate $\times 10^3$ M	$k_{\text{N}_3^-}/k_{\text{CN}^-}$
Ph ₃ CCl	Substrate added to nuc.	1.35	2.17
	Nuc. added to substrate	1.35	2.1
Ph ₃ CBr	Substrate added to nuc.	4.0	2.1
	Nuc. added to substrate	4.0	2.1
Ph ₃ CClO ₄	Substrate added to nuc.	4.0	0.98
	Nuc. added to substrate	4.0	0.32
	» » » »	1.35	1.54

not be neglected. The dependence of rates of reactions of triphenylmethyl halides upon the displaced halide ion was first recognized by Hill.³³

In Table 3 are listed the results from some competition experiments performed with various reagent concentrations and in Table 4 are the experimentally determined competition ratios when the mixture of the nucleophiles was added to the substrate and *vice versa*.

The results in Tables 3 and 4 suggest that competition experiments toward weakly dissociated substrates may well be performed under differing experimental conditions. However, toward triphenylmethyl perchlorate, a completely dissociated substrate, various results may be obtained depending upon concentrations of reactants and experimental procedure. The significant change in the competition ratios upon a change in the concentration of triphenylmethyl perchlorate suggests that the electrophilic nature of the reacting species for this substrate is concentration dependent, but no explanation for this experimental fact is available at the present stage. In any event, the results in Tables 3 and 4 clearly indicate that detailed discussions based upon a limited number of experiments should be avoided.

In Tables 5, 6 and 7 are listed the results from competition experiments toward 4,4'4''-trimethoxytriphenylmethyl chloride in the presence of various amounts of lithium perchlorate, tetraphenylarsonium perchlorate, and tetraphenylarsonium chloride, respectively.

The results from the competition experiments in the presence of the various salts, Tables 5 to 7, can be summarized as follows:

1. The presence of lithium perchlorate and tetraphenylarsonium perchlorate (both salts increasing the dissociation of the alkyl halide)

Table 5. The effect of lithium perchlorate upon $k_{N_3^-}/k_{CN^-}$ and $k_{N_3^-}/k_{OCN^-}$. The substrate is (*p*-MeOPh)₃CCl.

(<i>p</i> -MeOPh) ₃ CCl × 10 ³ M	LiClO ₄ × 10 ⁴ M	$k_{N_3^-}/k_{CN^-}$	$k_{N_3^-}/k_{OCN^-}$
1.34	0.00	1.41 ± 0.08	1.87 ± 0.1
1.34	0.60	1.43	2.15
1.34	2.00	1.50	2.49
1.31	6.00	1.91	3.23
1.31	16.0	2.32	3.70
1.31	180	3.75	≈ 12

Table 6. The effect of tetraphenylarsonium perchlorate upon $k_{N_3^-}/k_{CN^-}$ and $k_{N_3^-}/k_{OCN^-}$. The substrate is (*p*-MeOPh)₃CCl.

(<i>p</i> -MeOPh) ₃ CCl × 10 ³ M	Ph ₄ AsClO ₄ × 10 ⁴ M	$k_{N_3^-}/k_{CN^-}$	$k_{N_3^-}/k_{OCN^-}$
1.34	0.00	1.41 ± 0.08	1.87 ± 0.1
1.28	0.33	1.47	2.45
1.28	0.67	1.58	
1.24	3.33	1.82	2.94
1.18	6.00	1.94	
1.23	16.5	2.08	
1.29	29.6	2.23	

Table 7. The effect of tetraphenylarsonium chloride upon $k_{N_3^-}/k_{CN^-}$ and $k_{N_3^-}/k_{OCN^-}$. The substrate is (*p*-MeOPh)₃CCl.

(<i>p</i> -MeOPh) ₃ CCl × 10 ³ M	Ph ₄ AsCl × 10 ⁴ M	$k_{N_3^-}/k_{CN^-}$	$k_{N_3^-}/k_{OCN^-}$
1.34	0.00	1.41 ± 0.08	1.87 ± 0.1
1.34	0.60	1.42	2.20
1.34	1.74	1.41	2.34
1.34	5.90	1.38	2.59
1.34	11.6	1.31	2.67
1.34	17.4	1.22	2.48
1.34	23.1		2.35
1.24	52.1	0.55	1.98

increases the trapping ability of the azide ion, especially relative to that of the cyanate ion. The effect is noticeable even for concentrations of these two salts considerably smaller than that of the substrate and thus the reacting nucleophiles. The effect of the cation appears to be negligible.

2. The presence of tetraphenylarsonium chloride, a source of the common ion, decreases only to a small extent the $k_{N_3^-}/k_{CN^-}$ ratio. Only for concentrations of tetraphenylarsonium chloride exceeding that of the substrate is this trend

significant. The $k_{N_3^-}/k_{OCN^-}$ ratios increase for concentrations of the ionic chloride up to that of the substrate, but then decrease.

DISCUSSION

As has been pointed out by Kovačević and co-workers,³⁴ the azide probe seems to yield useful mechanistic informations in two extreme cases, *i.e.* direct displacement reactions (S_N2) and when carbenium ions are the only possible reacting species. Since the relative ability of

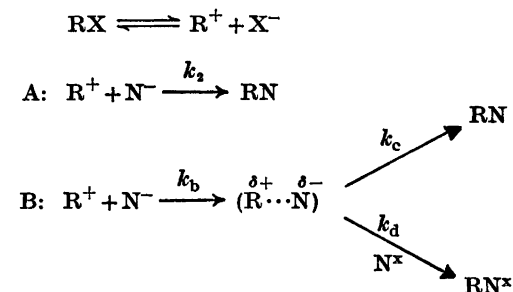
the various ions to compete for slightly dissociated substrates, like triphenylmethyl chloride and triphenylmethyl bromide, is about the same as when the completely dissociated triphenylmethyl perchlorate is employed as the substrate, the triphenylmethylcarbenium ion can not possibly be the reacting species in the present competition experiments (Table 2). The significant influence of the leaving group in the triphenylmethyl halides upon the competition ratios may be considered as additional evidence against the triphenylmethylcarbenium ion being the reacting species. According to Kovačević,³⁴ the azide ion should therefore not show any exceptional preference for the triarylmethyl substrates in acetonitrile as experienced in the present study.

As shown in the Experimental Part, the addition of a salt of a non-nucleophilic anion to a solution of a triphenylmethyl halide in acetonitrile, causes a rapid increase of the concentration of the triphenylmethylcarbenium ion, Ph_3C^+ . Salts of nucleophilic ions, on the other hand, cause a rapid reduction in the concentration of the triphenylmethylcarbenium ion. None of the examined reactions was sufficiently slow to be followed by the stopped-flow technique.

These unsuccessful kinetic studies allow one to propose that when ionic species are added to solutions of triphenylmethyl substrates in acetonitrile, the equilibria between the various possible species²⁻⁵ are set up extremely rapidly. This reorganization of the various species may well be the first step in reactions of triarylmethyl substrates in acetonitrile. As a prerequisite for this mechanism, the energy required for the transformation of colourless species, as ion pairs of various types, presumably tetrahedral and thus sp^3 hybridized, to coloured sp^2 hybridized carbenium ions containing coplanar central bonds³⁵ and *vice versa* must be very low. The facile dissociation of triarylmethyl substrates in a number of solvents suggests this to be the case. The repeatedly documented stability of triarylmethyl carbenium ions which do not contain stabilizing substituents may well be due to an effect of the lattice in the case of crystalline salts of carbenium ions and due to the solvating power of the solvent when the usual protic solvents are employed.³⁶

In acetonitrile, these stabilizing effects are largely absent and the stability of the triarylmethylcarbenium ions in this solvent relative to the various ion pairs is probably very low. In a reaction between a triarylmethyl substrate and a nucleophilic anion, the species first formed by the very rapid deionization step may well be the actual electrophilic species in the consecutive reaction (s) by which the final product is formed. Since the species formed through the deionization step are presumably far less selective toward the various nucleophiles than are the free or solvated carbenium ions, the reaction between the weakly separated species formed in the first step and the various nucleophiles is rapid and $k_{\text{N}_1}/k_{\text{N}_2}$ ratios close to unity are observed. The fact that ion pairs may well be considerably less selective than are free and solvated carbenium ions was first recognized by Ritchie.³⁷

The mechanism for the reaction between a completely dissociated triarylmethyl substrate, RX , and a nucleophilic anion N^- , may thus be as depicted in the following scheme.



In the case of reactions with triarylmethyl substrates, which yield stabilized carbenium ions as do triarylmethyl substrates containing *p*-dimethylamino substituents, k_b and k_c are negligible compared with k_2 . No deionization takes place due to the stability of the carbenium ion and the carbenium ion alone is the electrophilic species. Second order kinetics are observed and the azide ion is at least three orders of magnitude more reactive than is the cyanide ion both in protic and aprotic solvents.¹³ For a recent review, see Ref. 36.

In reactions of triarylmethyl substrates which do not contain substituents capable of exerting a stabilizing effect upon the corresponding carbenium ions, as the substrates used in the

present work, k_2 is considerably smaller than k_b and k_c . (The carbenium ions are consumed nearly entirely in the deionization step and will have negligible influence on the product composition.) The last step in B may be either an intramolecular rearrangement from an ion pair to the stable product or, in view of the small selectivity of ion pairs as suggested by Ritchie,³⁷ k_d is considerably greater than k_c and the final step is thus a displacement reaction. The fact that the trapping ratios when triphenylmethyl perchlorate was the substrate were found to be a function of experimental procedure may be due to varying degree of deionization.

In the case of slightly dissociated substrates, *i.e.* triarylmethyl halides, the deionization of the minute amount of carbenium ions will take place in the first step as for completely dissociated substrates. Ionization of these substrates is actually inhibited by the halide ions prior to the addition of the competing nucleophiles. This effect is the probable reason for the very limited dissociation of these substrates in acetonitrile (see Experimental Part). Since ion pairs of approximately the same type are obtained from completely dissociated substrates in the presence of nucleophilic anions and from slightly dissociated substrates due to the deionizing effect of the nucleophilic counter ions, the same trapping ratios are to be expected for the two classes of substrates, in agreement with the results of the present study.

In Table 8 some experimentally determined k_{N_1}/k_{N_2} ratios are compared with values obtained by multiplying the k_{N_1}/k_{N_2} and k_{N_2}/k_{N_3} ratios. The excellent agreement between the observed and calculated competition ratios may

be considered as additional evidence for a common mechanism B in the studied reactions.

Upon the addition of increasing amounts of the ionizing perchlorate, Tables 5 and 6, the k_{N_2}/k_{CN^-} ratio and especially the k_{N_2}/k_{OCN^-} ratio is seen to increase. This suggests that, in the presence of this non-nucleophilic anion, the deionization due to the competing nucleophilic anions does not completely suppress the carbenium ions and some product may then be formed by mechanism A, *i.e.* through reaction between carbenium ions and the nucleophilic anions. The trend in the competition ratios in Tables 5 and 6 clearly indicate that, when free carbenium ions are available as electrophilic species, the relative reactivity of the anions toward triarylmethylcarbenium ions is $N_3^- > CN^- > OCN^-$, in agreement with the usual reactivity sequence toward carbenium ions.¹⁸ Upon addition of the deionizing chloride ion, Table 7, a small decrease of the k_{N_2}/k_{CN^-} ratio is observed, suggesting that the reaction depicted by A is even more depressed.

The finding that the k_{N_2}/k_{CN^-} ratios decrease with increasing dissociation constants of the triarylmethyl substrates, Table 2, deserves some further comment. It is highly probable that, due to the extreme reactivity of azide ions toward carbenium ions, the majority of the ion pairs formed from the carbenium ions in the deionization step are ion pairs from the carbenium and azide ions. Less free azide ions will thus be left in the solution and, if the final step in mechanism B is a displacement reaction, the formation of organic cyanides will be favoured.

The deionization mechanism as suggested above for the first step in the reaction between

Table 8. Comparison between k_{N_1}/k_{N_2} determined experimentally and from the product of k_{N_1}/k_{N_2} and k_{N_2}/k_{N_3} .

Substrate	k_{N_2}/k_{CN^-}	Calc. ^a	k_{OCN^-}/k_{CN^-}	Calc. ^b
	Observed		Observed	
Ph ₃ CCl	2.17 ± 0.06	2.03 ± 0.18	1.52 ± 0.06	1.56 ± 0.05
Ph ₃ CBr	1.81 ± 0.09	1.56 ± 0.16	1.25 ± 0.06	1.29 ± 0.04
Ph ₃ CClO ₄	1.54 ± 0.09	1.78 ± 0.18		
(<i>p</i> -MePH) ₃ CCl	1.57 ± 0.09	1.49 ± 0.15		
(<i>p</i> -MeOPh) ₃ CCl	1.41 ± 0.08	1.32 ± 0.12		

^a k_{N_2}/k_{CN^-} (calc.) = $k_{N_2}/k_{OCN^-} \times k_{OCN^-}/k_{CN^-}$ (Table 2).

^b k_{OCN^-}/k_{CN^-} (calc.) = $k_{OCN^-}/k_{SCN^-} \times k_{SCN^-}/k_{CN^-}$ (Table 2).

triarylmethyl substrates and nucleophilic anions demands that carbenium ions are destabilized relative to the less dissociated ion pairs in the presence of nucleophilic species. From a purely electrostatic point of view the opposite effect is to be expected. The only possible explanation for the deionization appears to be a stabilization of weakly dissociated species relative to carbenium ions through interaction between the nucleophilic anions and the phenyl groups favouring sp^3 hybridized species at the expense of sp^2 hybridized planar carbenium ions. In protic solvents the nucleophilic anions due to their solvation shell will not exert this effect and the triarylmethylcarbenium ions, stabilized by these solvents, are the electrophilic species favouring the formation of triarylmethyl azides.

Recent magnetic resonance studies on triarylmethylcarbenium ions have revealed that only 25 to 30 % of the positive charge resides on the central carbon atoms, the remaining charge being located in the phenyl groups, notably in the *para*-positions.³⁸ It is highly possible that in triarylmethylcarbenium ions which do not contain stabilizing substituents, this delocalization of positive charge is sufficient to make the central carbon atom in the ion pair to act as a more attractive electrophilic center for the nucleophilic species than the central carbon atom in the carbenium ion.

The consequences of the suggested deionization mechanism on salt effects in S_N1 reactions are obvious. When carbenium ions or related species are the only possible intermediates in a reaction, and these intermediates are not sufficiently stabilized by the solvent, nucleophilic species may exert very negative salt effects.⁹⁻¹⁰ The deionization mechanism may also be the reason why highly erratic salt effects are observed even in protic solvents.⁷ In line with the suggestion that the deionization mechanism is only operative in reactions of substrates with delocalized charge on the corresponding carbenium ion it is interesting to note that very small and even negative b -values in the Winstein equation^{1,2,6} are observed only when the reacting substrate contains several phenyl groups.^{7,10}

The special effect observed in the present study may be general in aprotic solvents, but since the solvation of the nucleophilic species appears to enter as an important factor, ef-

fects of various magnitude may be observed. In this context it is interesting to note that triphenylmethyl halides have greatly varying dissociation constants in the various dipolar aprotic solvents.^{20,39} This suggests that trapping ratios, salt effects *etc.* in reactions of triarylmethyl substrates may vary from one dipolar solvent to another.

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REFERENCES

1. Ritchie, C. D. In Coetzee, J. F. and Ritchie, C. D., Eds., *Solute-Solvent Interactions*, Marcel Dekker, New York and London 1969, p. 272.
2. Winstein, S., Kleindienst, P. E., Jr. and Robinson, G. C. *J. Amer. Chem. Soc.* **83** (1961) 885.
3. Eigen, M. *Discuss. Faraday Soc.* **24** (1957) 25.
4. Atkinson, G. and Kor, S. K. *J. Phys. Chem.* **71** (1967) 673.
5. Olah, G. A. *J. Amer. Chem. Soc.* **94** (1972) 808.
6. Winstein, S., Appel, B., Baker, R. and Diaz, A. *Chemical Society (London) Special Publication*, **19** (1965) 109.
7. Bunton, C. A., Del Pesco, T. W., Dunlop, A. M. and Yang, K.-U. *J. Org. Chem.* **36** (1971) 887.
8. Ceccon, A., Fava, A. and Papa, J. *J. Amer. Chem. Soc.* **91** (1969) 5547.
9. Loupy, A. and Seyden-Penne, J. *C. R. Acad. Sci. Ser. C* **273** (1971) 1665.
10. Austad, T. and Songstad, J. *Acta Chem. Scand.* **26** (1972) 3141.
11. Parker, A. J. *Chem. Rev.* **69** (1969) 1.
12. Braunmann, J. I. and Archie, W. C., Jr. *J. Amer. Chem. Soc.* **92** (1970) 5891.
13. Ritchie, C. D., Shiner, G. A. and Badding, V. G. *J. Amer. Chem. Soc.* **89** (1967) 2063.
14. Fava, A., Iliceto, A., Ceccon, A. and Koch, P. *J. Amer. Chem. Soc.* **87** (1965) 1045.
15. Darwish, D. and Preston, E. A. *Tetrahedron Lett.* (1964) 113.
16. Austad, T., Songstad, J. and Åse, K. *Acta Chem. Scand.* **25** (1971) 331.
17. Austad, T., Songstad, J. and Stangeland, L. *J. Acta Chem. Scand.* **25** (1971) 2327.
18. Lorand, J. P. and Bartlett, P. D. *J. Amer. Chem. Soc.* **88** (1966) 3294.
19. Mayer, U. and Gutmann, V. *Monatsh. Chem.* **102** (1971) 148.
20. Longworth, W. R. and Mason, C. P. *J. Chem. Soc. A.* (1966) 1164.
21. Davies, G. L., Hay, D. H. and Wilkams, G. H. *J. Chem. Soc.* (1956) 4397.
22. Stangeland, L. J., Austad, T. and Songstad, J. *Acta Chem. Scand.* **27** (1973) 3919.

23. Bacon, R. G. R., Köchling, J. and Robinson, T. A. *J. Chem. Soc.* (1964) 5600.
24. Bentley, A., Evans, A. G. and Halpern, J. *Trans. Faraday Soc.* (1951) 711.
25. Zanella, P. and Tagliani, G. *J. Organometal. Chem.* 12 (1968) 355.
26. Plazzogna, G., Zanella, P. and Doretto, L. *J. Organometal. Chem.* 29 (1971) 169.
27. Springer, C. H., Coetzee, J. G. and Kay, R. L. *J. Phys. Chem.* 73 (1969) 471.
28. Popov, A. I. and Humphrey, R. E. *J. Amer. Chem. Soc.* 81 (1959) 2043.
29. Raber, D. J., Harris, J. M., Hall, R. E. and v. R. Schleyer, P. *J. Amer. Chem. Soc.* 93 (1971) 4821 and 4829.
30. Austad, T., Engemyr, L. B. and Songstad, J. *Acta Chem. Scand.* 25 (1971) 3536.
31. Engemyr, L. B. and Songstad, J. *Acta Chem. Scand.* 26 (1972) 4179.
32. Miotti, U. and Ceccon, A. *Ann. Chim. (Rome)* 54 (1964) 851.
33. Hill, E. A. *Chem. Ind. (London)* (1965) 1696.
34. Kovačević, D., Majerski, Z., Borčić, S. and Sunko, D. E. *Tetrahedron* 28 (1972) 2469.
35. Andersen, P. and Klewe, B. *Acta Chem. Scand.* 19 (1965) 791.
36. Ritchie, C. D. *Accounts Chem. Res.* 5 (1972) 348.
37. Ritchie, C. D. *J. Amer. Chem. Soc.* 93 (1971) 7324.
38. Ray, G. J., Kurland, R. J. and Colter, A. K. *Tetrahedron* 27 (1971) 735.
39. Pocker, Y. *J. Chem. Soc.* (1958) 240.

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