Solvent Properties of Dichloromethane. 1. The Reactivity of Dichloromethane toward Some Ionic Nucleophiles. Dichloromethane as Solvent for Finkelstein Reactions

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The reactions of dichloromethane with various pseudohalide ions, N_3^-, NC^-, $NCTe^-$, $NCSe^-$, NCS^- and OCN^-, have been studied kinetically under homogeneous conditions in dichloromethane as solvent at 25.0 °C. In the 10^{-3} M concentration range the half-lives of the reactions are 70 min(N_3^-), 80 min(NC^-), 15 h($NCTe^-$), 60 h($NCSe^-$), 400 h(NCS^-) and 600 h(OCN^-). 1,2-Dichloroethane in 1,2-dichloroethane is slightly more reactive toward N_3^- and NCS^- with half-lives of 60 min and 150 h, respectively. CH_2Br_2 in CH_2Br_2 is 400 times as reactive as is CH_2Cl_2 in CH_2Cl_2 toward NCS^-; half-life 60 min.

The homogeneous Finkelstein reactions between methyl iodide and NCS^- and Cl^- in CH_2Cl_2 were studied kinetically at 25.0 °C. For equal initial concentrations of NCS^- (1.2×10^{-2} M) the reactivity order is [PNP]SCN>Ph₄AsSCN>Bu₄NSCN as anticipated from their association constants in CH_2Cl_2. When corrected for ion-pairing the second order rate constants are fairly independent of the counterion. The MeI-NCS^- and the MeI-Cl^- reactions proceed as rapidly in dichloromethane as in the usual dipolar aprotic solvents of considerably higher dielectric constants. The relative uncorrected second order rate constants for the MeI-NCS^- reaction in CH_2Cl_2, in 1,2-dichloroethane and in 1,1,2,2-tetrachloroethane are 1:0.8:0.2 at 25.0 °C.

Halogenated alkanes and especially dichloromethane have for a long time been used as solvents in synthesis and also as extraction agents due to their excellent solvent properties.[1] With the advent of synthetic procedures based upon phase-transfer catalysis[2-4] in which dichloromethane is the favourite organic co-solvent the

use of this solvent has been greatly increased. In recent years, dichloromethane has also become a most useful solvent in inorganic chemistry since inorganic complexes which contain ligands with large organic groups, particularly aromatic groups, are readily soluble in this solvent.[5] Of no less importance is the general availability of this solvent, its low price and its fairly simple purification. When properly stored this solvent can be kept for months without decomposition.

However, all solvents have both their advantages and their disadvantages and dichloromethane is certainly not an exception to this rule. In this series we report on some of the characteristic properties of dichloromethane with special emphasis on its reactivity toward various species which causes some obvious limitations in its use as a solvent. Furthermore, its potential as solvent for various substitution reactions will be examined. For comparison other halogenated alkanes will also be considered.

In the present study we report on the reactivity of some anionic nucleophiles toward dichloromethane in dichloromethane as solvent. Purely nucleophilic species, N, are known to react by two consecutive nucleophilic displacement reactions[6,7] as shown by eqns. (1) and (2).

$$CH_2Cl_2 + N \xrightarrow{k_{2,1}} ClCH_2N + Cl^- \qquad (1)$$

$$ClCH_2N + N \xrightarrow{k_{2,2}} NCH_2N + Cl^- \qquad (2)$$
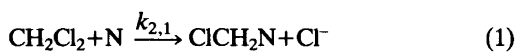
Presently, no detailed information is available with regard to the relative reactivity of $ClCH_2Cl$

and $ClCH_2N$ toward nucleophiles, *i.e.* $k_{2,1}$ and $k_{2,2}$. $PhSeCH_2Cl$ is suggested to be more reactive toward $PhSe^-$ than is $ClCH_2Cl$ [8] and for equal concentrations of $ClCH_2Cl$ and N in various solvents the final product, NCH_2N, is the major one; however, some exceptions are known.[6,7] In the majority of the reactions with nucleophiles performed under phase-transfer catalysis conditions the bis-product, NCH_2N, is the predominant one, but this may be due to prolonged reaction times.[9] In the reaction between diiodomethane and amines the second step is known to be the slower one.[10] In the present study in which [N], and thus $[ClCH_2N]$, was maximally 10^{-3} of that of the solvent, 15.50 M at 25.0 °C, one may safely assume the second step to be kinetically unimportant.

The reactivity of some pseudohalide ions, N_3^-, NC^-, $NCTe^-$, $NCSe^-$, NCS^- and NCO^- were studied under homogeneous conditions. These anions were chosen since the IR technique using liquid cells of various path lengths allowed rate constants to be determined with fairly high accuracy in different concentration ranges.[11-13] Data for the reactivity of most of these ions toward alkyl halides in various protic and aprotic solvents are available [11,14] allowing valuable comparisons to be made. As sources for the anions were used Bu_4NX, Ph_4AsX and $[(Ph_3P)_2N]X$; the latter abbreviated [PNP]X. Recently, association constants, K_A, for several of these salts in dichloromethane at 25.0 °C have been determined.[15,16] The corrected second order rate constants, $k_{2,1}$ (corr.), for some of the reactions could thus be calculated.

The limited reactivity of the thiocyanate ion toward dichloromethane allowed a kinetic study of the classical Finkelstein reaction between this ion and methyl iodide in this solvent, eqn. (3).

$$MeI + NCS^- \xrightarrow{ClCH_2Cl} MeSCN + I^- \qquad (3)$$

When corrected for association of the various ionic thiocyanates, the corrected second order rate constant in dichloromethane could be calculated. A comparison could thus be made with rate constants in other solvents. A similar study was also performed on the reaction between methyl iodide and chloride ion, eqn. (4).

$$MeI + Cl^- \xrightarrow{ClCH_2Cl} MeCl + I^- \qquad (4)$$

EXPERIMENTAL

Purification of dichloromethane. Dichloromethane, *technical grade*, was vigorously stirred for several days with small portions of concentrated sulfuric acid, 50 ml *per.* 5 l solvent, until the acid was colourless. The solvent was then washed with water until all acid had been removed, then vigorously stirred for some hours with 3 portions of 100 ml 1 M Na_2CO_3 and finally with distilled water of pH 6 until a neutral aqueous solution had been obtained. After drying with anhydrous $CaCl_2$, then with anhydrous K_2CO_3 and finally with CaH_2, the solvent was fractionated from CaH_2 in a dry argon atmosphere with a column of ~30 theoretical plates, b.p. 40.0–40.5 °C. The first and the last 10 % were discarded leaving a total yield of 3.5 l from 5 l. The purified product was stored over freshly activated Linde Molecular Sieves (4 Å) in 1/4 and 1/2 l bottles in darkness at −30 °C. No silicon grease was used during the purification process or during storage.

Several attempts were performed by GLC by various columns to analyze the purity of the solvent; however, no exact measure could be obtained. The ^1H NMR spectrum and the ^{13}C NMR spectrum (30000 accumulations) did not indicate any impurities; for comparison, dichloromethane contaminated with 1 % pentane or 1 % hexane gave distinct ^1H and ^{13}C signals. The specific conductivity of the solvent was less than 8.4×10^{-10} S cm^{-1} which was the lower limit of the conductivity equipment. No decomposition could be detected as viewed by kinetic results, by NMR spectra or by conductivity studies after several months when the purified solvent was stored as described above. No definite advantages with regard to the quality of the purified product could be observed when starting out from *p.A.* qualities instead of *technical grade*.

Halogenated solvents and reagents. Methyl iodide, Fluka *purum*, was washed with several portions of 5 % aqueous solution of K_2CO_3, then with water and was finally dried with anhydrous K_2CO_3. After filtration, the reagent was fractionated and stored in a black-painted bottle at −10 °C. 1,1,2,2-Tetrachloroethane, J. T. Baker, *Baker Grade*, was purified in a similar way and distilled twice prior to use. Dibromomethane, Koch-Light Labs., *puriss*, was flushed with argon for 2 h to remove traces of HBr and then distilled twice. 1,2-Dichloroethane, *Merck Spectroscopic Grade*, was fractionated from CaH_2 prior to use. Midfractions of the solvents were used for the kinetic studies.

Onium salts. The preparation and purification of the bis(triphenylphosphine)iminium salts,

[PNP]X, (X=NCSe$^-$, NCTe$^-$, NCO$^-$, N$_3$$^-$, NC$^-$, NCS$^-$, Cl$^-$ and I$^-$) and tetraphenylarsonium thiocyanate, Ph$_4$AsSCN, was performed as previously described.[11,12,17] Tetramethylammonium thiocyanate, Me$_4$NSCN, was made from the corresponding chloride and dried KSCN in dry acetone and crystallized from this solvent and finally from acetonitrile, m.p. 293–296 °C (296–297 °C [18]). This salt was only used for the solubility study. Tetrabutylammonium thiocyanate, Bu$_4$NSCN, was made from the corresponding nitrate and dry KSCN in dry methanol. The salt was crystallized several times from ethyl acetate–hexane, m.p. 118–119 °C (119–120 °C [19]).

Solubility of onium thiocyanates in dichloromethane. Me$_4$NSCN: 100 ml of dichloromethane containing excess salt was stirred for 20 h at 25.0 °C; 20 h amount to only some 5 % of the half-life of the reaction. After filtration the solvent was removed in vacuum and the residue dissolved in 10 ml acetone. The concentration of ionic thiocyanate was determined by IR at 2058 cm^{-1} using 0.1 cm liquid cells and a calibration curve between peak height at this wave length *versus* the concentration of SCN$^-$ in acetone. Bu$_4$NSCN: a saturated but very viscous solution was obtained at 25.0 °C, the concentration of which was determined by IR as for Me$_4$NSCN after 500 times dilution. Ph$_4$AsSCN and [PNP]SCN: saturated solutions could not be obtained; the solutions turned only more and more viscous upon addition of more salts allowing only minimum solubilities to be estimated.

Determination of rate constants. In Table 1 are listed some IR and UV data for the various compounds which formed the basis for the analytical methods for the determination of the rate constants. Also in Table 1 are listed the association constants, K_A, for the ionic thiocyanates and for some [PNP]-salts from a recent conductivity study.[16]

All reactions of dichloromethane with the pseudohalide ions, except the cyanide ion, were followed directly by IR in the 2000–2200 cm^{-1} region using liquid cells, *cf.* first column in Table 1. The reactions of N$_3$$^-$, NCS$^-$ and NCSe$^-$ were examined in both the 10^{-3} and the 10^{-2} M concentration range, the CH$_2$Cl$_2$-NCTe$^-$ reaction only in the 10^{-3} M range owing to the limited solubility of [PNP]TeCN. Several attempts were made to follow the CH$_2$Cl$_2$-OCN$^-$ reaction also in the 10^{-2} M range but poor and non-reproducible kinetics were observed in this concentration range.

The CH$_2$Cl$_2$-NC$^-$ reaction could not be followed directly by IR owing to the very small extinction coefficient of the cyanide ion at 2060

Table 1. IR, UV and association data in dichloromethane at 25.0 °C which formed the basis for the analytical methods applied for the determination of the second order rate constant.

	ν_{max}(cm^{-1})[a]	ε(250.5 nm)	$K_A \times 10^{-3}$ (1 M^{-1})[c]
N$_3$$^-$	2005		
NCTe$^-$	2081		
NCSe$^-$	2067		
NCS$^-$	2058[b]		
OCN$^-$	2140		
MeI		3.71×10^2	
I$^-$		1.08×10^4	
[PNP]$^+$		3.34×10^3	
Ph$_4$AsSCN			3.3(2)
Bu$_4$NSCN			27(5)
[PNP]Cl			1.7(3)
[PNP]SCN			1.8(2)
PNP]SeCN			1.2(2)
[PNP]OCN			1.5(2)
[PNP]CN			~0.5(1)

[a] Within experimental error, ± 2 cm^{-1}, the same frequencies as observed in acetonitrile, *cf.* Ref. 12. [b] In dibromomethane, in 1,2-dichloroethane and in 1,1,2,2-tetrachloroethane ν_{max} for NCS$^-$ was also observed at 2058(2) cm^{-1}. [c] From Ref. 16.

cm^{-1}. The amount of unreacted ionic cyanide was therefore determined at appropriate time intervals as the selenocyanate ion by IR at 2067 cm^{-1} after selenization with a slight excess, 5 %, of triphenylphosphine selenide dissolved in a known volume of acetonitrile. Prior to the addition of the selenating agent, the solvent was rapidly removed in vacuum and the residue washed with diethyl ether. This change of solvent from dichloromethane to acetonitrile prior to the addition of Ph$_3$PSe was necessary since the equilibrium constant for the very rapid Ph$_3$PSe-NC$^-$ reaction in dichloromethane forming Ph$_3$P and NCSe$^-$ was found to be only 18(2) for a concentration of [PNP]CN of 3×10^{-2} M. In acetonitrile, the corresponding equilibrium constant is very large, ≫100, as viewed from IR studies of the reverse reaction, Ph$_3$P-NCSe$^-$, using a large excess of Ph$_3$P. Control experiments showed this method to determine concentrations of ionic cyanide in dichloromethane to be quantitative within 3 %.

The CH$_2$Cl$_2$-NC$^-$ reaction mixture in the 10^{-3} M range attained after 2h, *i.e.* 2 half-lives, a slight yellow colour; after 24 h a weak pink colour could be observed. In the 10^{-2} M range this colourization of the reaction mixture was more

rapid and the rate constant for this reaction was therefore only determined in the 10^{-3} M range. All experiments involving [PNP]CN and [PNP]TeCN were performed in solvent batches carefully flushed with argon.

The MeI-NCS$^-$ reactions in dichloromethane, in 1,2-dichloroethane, and in 1,1,2,2-tetrachloroethane were also followed by IR. These reactions were studied under second order conditions with equal initial concentrations of MeI and of NCS$^-$, 1.2×10^{-2} M. Separate experiments showed the reactions of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane with NCS$^-$ to be sufficiently slow at 25.0 °C, cf. Table 2. The reaction between [PNP]Cl and methyl iodide in dichloromethane was also studied under second order conditions with initial concentrations of 1.2×10^{-2} M. The rate constant was calculated from the increase in absorption with time at 250.5 nm after the necessary dilution had been done. A distinct well in the absorption curve of the [PNP]-cation at this particular wavelength[17] made this rate determination possible, cf. Table 1. All rate constants were calculated from measurements performed at 25.0(1) °C. Up to 8 aliquots were withdrawn periodically for each kinetic run. With the exception of the CH$_2$Br$_2$-NCS-reaction all reactions were studied at least in duplicate and with separate weighing of the reactants.

Calculations. For the reaction between dichloromethane and an ionic nucleophile in dichloromethane as solvent as depicted by eqns. (1) and (2), pseudo-first order conditions exist since [CH$_2$Cl$_2$]>10^3[N]. When disregarding association and assuming the reaction according to eqn. (2) to be of no kinetic importance, the usual pseudo-first order equation is valid, eqn. (5).

$$\ln[a/(a-x)]=k_{2,1}Bt \qquad (5)$$

a is the initial concentration of the nucleophile, N, x is the concentration of products at time t and B is the molar concentration of CH$_2$Cl$_2$, 15.50 M at 25.0 °C. All kinetic runs were analyzed according to this rate equation and excellent rate plots were observed for more than 3 half-lives except for the CH$_2$Cl$_2$-OCN$^-$ reaction in the 10^{-2} M concentration range as mentioned above. Attempts to include the reaction as depicted by eqn. (2) in the kinetics, i.e. $k_{2,2}x \sim k_{2,1}B$, caused significant curvature in the rate plots.

When taking association of the applied salts into account one may assume that there is no change in the association constant K_A during the reaction. This approximation may be justifiable since constant ionic strength is maintained during the kinetic runs and association constants of salts of large cations and small anions in dichloro-

methane are fairly independent upon the anion, cf. Table 1. When neglecting higher order aggregates[20] and also assuming the ion pairs to be non-reactive, the following rate equation is valid, eqn. (6).

$$-dx/dt=k_2B(2K_A)^{-1}[(1+4K_A(a-x))^{1/2}-1] \qquad (6)$$

k_2 is the second order rate constant corrected for association, $k_{2,1}$ (corr.), and $k_{2,2}$ is neglected as in eqn. (5). Upon integration one obtains

$$M=-k_2Bt+C \qquad (7)$$

in which

$$M=(1+4K_A(a-x))^{1/2}+\ln[(1+4K_A(a-x))^{1/2}-1]$$

and

$$C=(1+4K_A)^{1/2}+\ln[(1+4K_Aa)^{1/2}-1].$$

In the case of the Finkelstein reactions, MeI-NCS$^-$ and MeI-Cl$^-$, eqns. (3) and (4), respectively, the usual second order rate equation applies for equal initial concentrations of the reactants when neglecting association, eqn. (8).

$$x/a(a-x)=k_2 \text{ (uncorr.) } t \qquad (8)$$

When taking association into account but, as above, no higher order aggregates[20] and also assuming the ion-pairs to be non-reactive, the rate equation is

$$dx/dt=k_2(2K_A)^{-1}[(1+4K_A(a-x))^{1/2}(a-x)] \qquad (9)$$

in which k_2 is k_2 (corr.).
Upon integration one obtains

$$Q=k_2(2K_A)^{-1}t+D \qquad (10)$$

in which

$$Q=[(1+4K_A(a-x)^{1/2}-1]^{-1}+\tfrac{1}{2}\ln[((1+4K_A(a-x))^{1/2}+1][(1+4K_A(a-x))^{1/2}-1]^{-1}$$

$$D=[(1+4K_Aa)^{1/2}-1]^{-1}+\tfrac{1}{2}\ln[(1+4K_Aa)^{1/2}+1]\times[(1+4K_Aa)^{1/2}-1]^{-1}$$

A general program was written and used for the calculation of the rate constants according to eqns. (7)−(10).

RESULTS AND DISCUSSION

Solubility of onium thiocyanates. The solubility of   tetramethylammonium   thiocyanate,

Me₄NSCN, in dichloromethane at 25.0 °C was found to be only 8.3×10^{-4} M dm³. The limited solubility of this salt is in general agreement with the results from solubility studies on various tetramethylammonium salts in 1,1- and 1,2-dichloroethane.[21,22] Tetramethylammonium salts can therefore in general not be used as sources of anions for homogeneous reactions in halogenated alkanes. Furthermore, owing to their limited solubilities in this class of solvents, tetramethyl-ammonium salts have low extraction constants and are therefore of limited use in phase-transfer catalysis,[23] cf. Ref. 2.

The solubility of Bu₄NSCN is approximately 5.7 M dm³ and this salt is thus close to four powers of ten more soluble in dichloromethane than is the corresponding Me₄N⁺-salt. This observation is also in agreement with solubility studies in the dichloroethanes.[21,22] Tetraalkylam-monium salts with symmetrical cations containing 16 or more carbon atoms are well known to be very soluble in solvents of fairly low dielectric constant and are also significantly better dissociated in this class of solvents than are tetraalkyl-ammonium salts with smaller alkyl groups.[2,24] Presumably, this increase in solubility of tetra-alkylammonium salts with increasing length of the carbon chain is due to the increase in the hydrophobicity of the cations per added CH₂ group[2] combined with the increasing ability of the larger cations to adapt configurations which enable a constant minimum cation−anion separation to be maintained.[25,26]

Ph₄AsSCN and [PNP]SCN are extremely soluble in dichloromethane at room temperature and only estimates of their solubilities in this solvent can be given, >6 M dm⁻³. Actually, only few salts of these two cations can be crystallized from dichloromethane alone. The exceptional solubility of salts of these cations and of other cations containing several phenyl or aryl groups and also of non-ionic aromatic compounds in general is presumably due to specific interaction between the π-electrons of the phenyl groups and the hydrogen atoms of the solvent.[15,27−30] In spite of the fairly low dielectric constant of dichloro-methane, 8.9 at 25.0 °C,[31,32] salts in which the cation or the anion contain several phenyl groups are readily dissolved in this solvent due to this unique solvation of the phenyl groups. As a result, these salts are also less associated in dichloromethane than are tetraalkylammonium

salts, cf. Refs. 15 and 16 and Table 1. Hydrogen bond formation plays apparently a seemingly small role in the solvation of halide ions and other small anions in dichloromethane and other halogenated alkanes.[15,21,22] Solubilization and dissociation of salts in dichloromethane and related solvents are thus not assisted by solvation of the anions leaving these fairly "naked".[24] However, as is to be outlined below, this conclusion may not be valid for strongly basic anions.

It should be emphasized that this special preference for aryl groups as observed for di-chloromethane is apparently not the case for 1,2-dichloroethane. Salts of phenyl-containing cations such as Ph₄P⁺ and Ph₄As⁺ are generally considerably less soluble in 1,2-dichloroethane than are the corresponding Bu₄N⁺-salts and are only some two powers of ten more soluble than are the corresponding Me₄N⁺-salts.[21,22] In this connection it is interesting to note that 1,2-di-chloroethane and benzene give a fairly ideal solvent mixture with a slightly endothermic heat of mixing.[33] The interaction between dichloro-methane and benzene, however, is exothermic and a non-ideal mixture is obtained.[33] 1,1-Dichloroethane exhibits even less solubilizing properties toward aromatic compounds than does 1,2-dichloroethane and Ph₄P⁺ and Ph₄As⁺-salts are generally significantly less soluble in this solvent than in the latter solvent.[21,22] From the thermodynamic parameters for the benzene-CH₂X₂ complexes[28] one may conclude that CH₂I₂ and CH₂Br₂ will behave fairly similarly toward phenyl-containing ions and aromatic com-pounds as does CH₂Cl₂.

The reactivity of dichloromethane toward the pseudohalide ions. In Table 2 are listed the second-order rate constants, $k_{2,1}$ (uncorr.), for the reactions between dichloromethane and the pseudohalide ions in dichloromethane at 25.0 °C. Table 2 also includes some rate constants of CH₂Br₂ and of 1,2-dichloroethane. [PNP]-salts were used as the source of the anions and the 10^{-3} M concentration range was common for all reactions. The listed second-order rate constants, $k_{2,1}$ (uncorr.), are uncorrected for ionic associa-tion, eqn. (5), and are based upon the molarity of the dihaloalkanes and not on the number of C−X bonds. For comparison with rate data of mono-haloalkanes, RX, the rate constants in Table 2 and thus also in Tables 3−5 will have to be divided by two. In the last two columns in Table 2

Table 2. Rate constants uncorrected for ionic association, $k_{2,1}$ (uncorr.), half lives, τ, and relative rate constants for the reactions between [PNP]X and CH_2Cl_2 in CH_2Cl_2, between [PNP]SCN and CH_2Br_2 in CH_2Br_2 and between [PNP]X and $ClCH_2CH_2Cl$ in $ClCH_2CH_2Cl$ at 25.0 °C.

X^-	Substrate solvent	Conc. range (M)	$k_{2,1}$ (uncorr.) $(M^{-1}s^{-1})$	τ(h)	Rel. rate [a]
N_3^-	CH_2Cl_2	10^{-3}	$1.09(4)\times10^{-5}$	1.13(5)	
		10^{-2}	$1.05(6)\times10^{-5}$	1.16(6)	300
NC^-	CH_2Cl_2	10^{-3}	$9.3(2)\ \times10^{-6}$	1.3(1)	270
$NCTe^-$	CH_2Cl_2	10^{-3}	$8.2(1)\ \times10^{-7}$	15(1)	24
$NCSe^-$	CH_2Cl_2	10^{-3}	$1.98(7)\times10^{-7}$	62(2)	6
		10^{-2}	$1.78(7)\times10^{-7}$	69(3)	
NCS^-	CH_2Cl_2	10^{-3}	$3.4(2)\ \times10^{-8}$	360(20)	1
		10^{-2}	$2.9(2)\ \times10^{-8}$	430(20)	
OCN^-	CH_2Cl_2	10^{-3}	$2.0(2)\ \times10^{-8}$	600(25)	0.6
NCS^-	CH_2Br_2	10^{-3}	$1.3(1)\ \times10^{-5}$	1.0(1)	360
NCS^-	$(ClCH_2-)_2$	10^{-3}	$1.0(2)\ \times10^{-7}$	153(15)	3
N_3^-	$(ClCH_2-)_2$	10^{-3}	$1.43(6)\times10^{-5}$	1.06(6)	360

[a] Rate constant for the NCS^--CH_2Cl_2 reaction in the 10^{-3} M concentration range defined as unity.

are listed the half-lives, τ, together with the relative rates of the reactions. (The rate constant for the CH_2Cl_2-NCS^- reaction in the 10^{-3} M concentration range is defined as unity.)

The data in Table 2 show that $NCTe^-$, $NCSe^-$, NCS^- and OCN^- react quite slowly with dichloromethane with half-lives ranging from 15 to 600 h at 25.0 °C. Dichloromethane and presumably also 1,2-dichloroethane may therefore prove to be important solvents for studies of these anions provided large aromatic cations or Bu_4N^+ are used. The half-lives for the CH_2Cl_2-N_3^- and CH_2Cl_2-NC^- reactions, however, are only some 70–80 min at room temperature which seriously limits the use of dichloromethane as solvent for studies of reactions involving these two ions. 1,2-dichloroethane is apparently not an alternative, *cf.* Table 3, last entry. Dibromomethane, CH_2Br_2, is 360 times as reactive as is dichloromethane toward the thiocyanate ion with a half-life of only some 60 min. The high reactivity of CH_2Br_2 toward carbophilic nucleophiles as experienced with NCS^- in the present study and also toward halophilic nucleophiles [34] suggests that CH_2Br_2 has only a limited potential as solvent for chemical reactions.

Table 3. A comparison between the second order rate constants for the MeI-X^- reactions in acetonitrile, k_2, and the corresponding uncorrected second order rate constants for the CH_2Cl_2-X^- reactions in dichloromethane in the 10^{-3} M range, $k_{2,1}$ (uncorr.), at 25.0 °C.

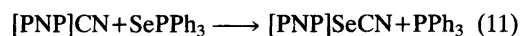| X^-	k_2[a] $(M^{-1}s^{-1})$	$k_{2,1}$(uncorr.)[b] $(M^{-1}s^{-1})$	$[k_{2,1}(\text{uncorr.})/k_2]\times10^6$
N_3^-	2.45×10^{-1}	1.1×10^{-5}	45
$NCTe^-$	~1.8[c]	8.2×10^{-7}	~0.4
$NCSe^-$	1.77×10^{-1}	2.0×10^{-7}	1.1
NCS^-	2.06×10^{-2}	3.4×10^{-8}	1.7
OCN^-	1.7×10^{-2}	2.0×10^{-8}	1.2
NC^-	26.5	9.3×10^{-6}	0.35

[a] From Ref. 13. [b] From Table 2. [c] Assuming the rate constant for the MeI-$NCTe^-$ reaction to be ten times the rate constant for the MeI-$NCSe^-$ reaction, *cf.* Ref. 12.

The association constants of [PNP]-salts in dichloromethane are fairly independent upon the anion.[15,16] Reactivities of anions in this solvent when [PNP]-salts are used may therefore be compared with reactivities in other solvents in which the applied salts are completely dissociated. Table 3 presents such a comparison between the rate constants as determined in the present study in the 10^{-3} M concentration range and the rate constants for the reactions between the anions and methyl iodide in acetonitrile at 25.0 °C. The ratios between the rate constants, last column in Table 3, show that the anions except the azide ion, N$_3^-$, and possibly the cyanide ion, NC$^-$, respond quite similarly to the change in both substrate and solvent although CH$_2$Cl$_2$ in CH$_2$Cl$_2$ is some six powers of ten less reactive than is MeI in MeCN.

The high rate of the CH$_2$Cl$_2$-N$_3^-$ reaction prevents accurate conductivity studies on ionic azides in dichloromethane to be performed. Since all [PNP]-salts, however, appear to have association constants in dichloromethane at 25.0 °C in the $1-2 \times 10^3$ M^{-1} range [16] one may conclude that the high reactivity of the azide ion in this solvent is not caused by an exceptionally low association constant of [PNP]N$_3$. The question therefore arises whether specific solvation of the anions in dichloromethane is a determining factor with regard to the reactivity of anions in this solvent. While NCTe$^-$, NCSe$^-$ and NCS$^-$, the three weakly basic and soft nucleophiles, may be solvated through the chlorine atoms,[35] the two basic anions, NC$^-$ and OCN$^-$, are presumably solvated through interaction with the hydrogen atoms. The high rate of the CH$_2$Cl$_2$-N$_3^-$ reaction may well be due to a poor interaction between the azide anion and the solvent molecules. The solvation of the azide ion in dichloromethane may differ from that of the cyanate ion since oxygen atoms seem to interact more strongly than nitrogen atoms with the hydrogen atoms of this solvent; cf. the thermodynamic studies on the R$_2$O-CH$_2$Cl$_2$ and the R$_3$N-CH$_2$Cl$_2$ adducts.[36,37] Oxygen nucleophiles like phenoxide ions [43] are known to be distinctly less reactive in dichloromethane than in the usual dipolar aprotic solvents while nitrogen nucleophiles like the azide ion and pyridine do not suffer a similar decrease in reactivity.[39] In short, dichloromethane and other halogenated alkanes seem to behave as protic solvents toward highly basic species, i.e.

the cyanide ion as mentioned above, and toward nucleophiles containing an oxygen atom, i.e. OCN$^-$ and ArO$^-$.[38] It is notable that ionic fluorides may be crystallized from dichloromethane without any reaction taking place.[17,40]

No data are presently available with regard to the acidity of dichloromethane. This compound is undoubtedly a very weak acid and is probably less acidic than is acetonitrile.[41,42] The mere fact that the tellurocyanate ion does not decompose in dichloromethane is evidence for the weakly acidic properties of this solvent.[43] The very basic cyanide ion does not seem to deprotonate dichloromethane to a significant extent since a freshly prepared solution of [PNP]CN in this solvent was found to give a quantitative yield of ionic selenocyanate after treatment with a slight excess of triphenylphosphine selenide in acetonitrile, cf. eqn. (11).

$$[PNP]CN + SePPh_3 \longrightarrow [PNP]SeCN + PPh_3 \quad (11)$$

Actually, the cyanide ion in dichloromethane is apparently not sufficiently basic to deprotonate even ClCH$_2$CN, the first formed product from the CH$_2$Cl$_2$-NC$^-$ reaction, to an extent which is kinetically detectable. If this were the case, a second molecule of ionic cyanide would be consumed leading to a rate equation as shown in eqn. (12).

$$\ln[a/(a-2x)] = 2k_{2,1}Bt \quad (12)$$

The rate data for the CH$_2$Cl$_2$-NC$^-$ reaction were in no case found to obey eqn. (12); all rate data could actually be treated successfully according to the usual rate equation, eqn. (5), for more than three half-lives. The weakly yellow colourization of the reaction mixture after some two half-lives, however, suggests that some deprotonation reactions take place. Proton transfer may also be the cause for the poor kinetics observed for the CH$_2$Cl$_2$-OCN$^-$ reaction in the more concentrated runs, cf. Experimental.

The equilibrium constants for the reaction as depicted by eqn. (11) are distinctly different in dichloromethane and in acetonitrile, 18(2) and $\geqslant 100$, respectively. The lower equilibrium constant in dichloromethane may partly be due to association of [PNP]CN in this solvent leaving fewer free cyanide ions available in dichloromethane than in acetonitrile. The lower equilib-

rium constant in dichloromethane, however, may be considered as further evidence for the suggestion that the cyanide ion is stabilized in this solvent. The fairly low estimate of the equivalent conductivity of the cyanide ion in dichloromethane [16] and the low association constant of [PNP]CN as compared with other [PNP]-salts, cf. Table 1, accord with this suggestion.

With regard to reactions of dichloromethane with nucleophiles, it should be emphasized that other factors than solvation of the nucleophiles may be responsible for the observed reactivity differences. The well documented reactivity decrease from monohalomethanes to dihalomethanes is generally supposed to be due to the polar effects of the halogen atoms and their steric demands to which the various nucleophiles respond differently.[44] The electronegative nature of the halogen atoms in dihalomethanes seems to favour attack by hard nucleophiles, cf. the considerable reactivity of amines, R_3N,[45] as compared with the poor reactivity of the generally very nucleophilic phosphines, R_3P.[45,46] The exceptional reactivity of the azide ion toward S_N1-type substrates is well-known, cf. the azide probe.[47] Since the steric demands of the one non-reacting halogen atom will prevent the formation of the ideal linear transition state, it is natural to assume that nucleophiles with small nucleophilic atoms are to be favoured. Recently [48] it has been suggested that the major interaction responsible for the deactivating effect of an α-chlorine substituent is the four-electron repulsion between a p-lone pair on the chlorine atom with the high-lying π-type orbital associated with the reaction coordinate at the S_N2 transition state. All factors taken into consideration the azide ion seems to be ideal for substitution

reactions with dihalomethanes. It is apparent that nucleophilicity scales derived from reactions with methyl halides [49] will be highly unreliable when attempting to predict the reactivity of nucleophiles toward dihalomethanes.

Ion-pairs, reactive or non-reactive? A mechanistically important question is whether the predominant nucleophiles in the CH_2Cl_2-X^- reactions are the ion-pairs of the free dissociated ions, cf. Refs. 2 and 50 for recent critical discussions of substitution reactions in solvents of low dielectric constants. Owing to the fairly large association constants of salts in dichloromethane, cf. Table 1, a considerable fraction of the anions do not exist as free dissociated ions but as ion-pairs. One of the basic assumptions made when evaluating the various rate equations for the CH_2Cl_2-X^- reactions was that the ion-pairs are non-reactive, cf. Experimental.

The uncorrected second order rate constants for the CH_2Cl_2-NCS^- and the CH_2Cl_2-$NCSe^-$ reactions as shown in Table 2 are slightly but probably significantly larger in the 10^{-3} M concentration range than in the 10^{-2} M range. This observation is as expected if the free dissociated anions were the predominant nucleophiles in the reactions. If the association constants of [PNP]SCN and [PNP]SeCN in dichloromethane were the same in the two concentration ranges and the second order rate constants were independent upon the ionic strength, the rate constant as calculated by eqn. (7) should be independent upon the concentration range provided the ion-pairs were non-reactive. As shown in Table 4, the corrected rate constants, k_2(corr.), for the CH_2Cl_2-NCS^- and the CH_2Cl_2-$NCSe^-$ reactions are significantly different. Apparently, one or several assumptions made when evaluat-

Table 4. Observed and uncorrected rate constants, $k_{2,1}$(uncorr.), and rate constants corrected for association, $k_{2,1}$(corr.), for the reaction between [PNP]SCN and [PNP]SeCN and CH_2Cl_2 in CH_2Cl_2 at 25.0 °C.

Conc. range	$k_{2,1}$(uncorr.)$\times 10^{8}$ [a] $(M^{-1}s^{-1})$	$k_{2,1}$(corr.)$\times 10^{8}$ [b] $(M^{-1}s^{-1})$
$10^{-2}(NCS^-)$	2.86(17)	31(2)
$10^{-3}(NCS^-)$	3.43(17)	14(1)
$10^{-2}(NCSe^-)$	17.8(7)	168(9)
$10^{-3}(NCSe^-)$	19.8(7)	67(4)

[a] Calculated according to eqn. (5). [b] Calculated according to eqn. (7).

ing eqn. (7) are not valid.

According to the Acree equation [51] an observed rate constant may be considered as the sum of the rates due to the free ions, k_i, and to the ion-pairs, k_m,[52-55] eqn. (13),

$$k_2 \text{(obs.)} = ak_i + (1-\alpha)k_m \qquad (13)$$

in which α, the degree of dissociation, is given by eqn. (14),

$$K_A = (1-\alpha)/c\alpha^2 \qquad (14)$$

and c is the concentration of the electrolyte. Since α is dependent upon the concentration, one may for the evaluation of k_i and k_m apply an average value of α as calculated from the average concentration of the applied salts during the kinetic runs for the two concentration ranges, 6×10^{-3} and 6×10^{-2} M, respectively. From the rate data in Table 4 the following rate constants may then be calculated; NCS$^-$: $k_i=6.0\times10^{-8}$ M^{-1}s^{-1} and $k_m=2.5\times10^{-8}$ M^{-1}s^{-1}; NCSe$^-$: $k_i=2.7\times10^{-7}$ M^{-1}s^{-1} and $k_m=1.7\times10^{-7}$ M^{-1}s^{-1}. Thus, the reactivity of the ion-pairs appears to be some 40 and 60 % of the reactivity of the free NCS$^-$ and NCSe$^-$ ions, respectively. Beronius and co-workers [52] have concluded that the nucleophilicity of the Bu$_4$N$^+$-Br$^-$ ion-pairs is some 20 % of the nucleophilicity of the free Br$^-$ ions toward 4-nitrobenzyl bromide in acetone. Since the k_i/k_m ratio is anticipated to decrease with decreasing dielectric constant of the solvent it may not be surprising to find that k_m is not negligible in a solvent like dichloromethane.

However, the numerous assumptions made when treating the kinetic data according to the Acree equation should be born in mind. Furthermore, the larger corrected rate constants in the 10^{-2} M range than in the 10^{-3} M range may be due to a positive salt effect and not to an increase in the relative concentration of the ion-pairs. Since no reliable data on salt effects on Finkelstein reactions in solvents of low dielectric constant are presently available, it is to be concluded that the Acree equation[5] is to be applied with caution for reaction systems of the type described in the present study. The ambiguity with regard to the possible reactivity of ion-pairs suggests that when rate data from kinetic studies involving weakly dissociated reactants are to be presented concentrations, counterions *etc.* are to be carefully listed in order to avoid futural invalid comparisons.

The MeI-NCS$^-$ and MeI-Cl$^-$ reactions. The results for these Finkelstein reactions are summarized in Table 5. In the first column are listed the uncorrected rate constants, k_2 (uncorr.), as calculated according to eqn. (8). In the last column are listed the corrected rate constant, k_2 (korr.), as calculated according to eqn. (10) when the necessary association constants were available.

As anticipated from the association constants, *cf.* Refs. 15 and 16 and Table 1, the uncorrected rate constant for the MeI-NCS$^-$ reaction is dependent upon the cation and increases from Bu$_4$NSCN to [PNP]SCN; Ph$_4$AsSCN being intermediate. When corrected for association fairly similar values for k_2 (corr.) are obtained, *cf.* the last column in Table 5. This observation suggests that the ion-pairs are fairly non-reactive toward

Table 5. Second order rate constants for the reactions between some onium thiocyanates and methyl iodide in CH$_2$Cl$_2$, between [PNP]SCN and methyl iodide in 1,2-dichloroethane and in 1,1,2,2-tetrachloroethane and between [PNP]Cl and methyl iodide in CH$_2$Cl$_2$ at 25.0 °C. (Initial concentrations of both reactants in the 1.14−1.25×10^{-2} M range).

Salt	Solvent	k_2(uncorr.)×10^2[a] (M^{-1}s^{-1})	k_2(corr.)×10^2[b] (M^{-1}s^{-1})
Bu$_4$NSCN	CH$_2$Cl$_2$	2.3(3)	25(5)
Ph$_4$AsSCN	CH$_2$Cl$_2$	4.5(3)	23(2)
[PNP]SCN	CH$_2$Cl$_2$	6.1(5)	23(2)
[PNP]SCN	C$_2$H$_4$Cl$_2$[c]	4.8(3)	[d]
[PNP]SCN	C$_2$H$_2$Cl$_4$[e]	1.27(8)	[d]
[PNP]Cl	CH$_2$Cl$_2$	14(2)	56(4)

[a] Calculated according to eqn. (8). [b] Calculated according to eqn. (10). [c] 1,2-Dichloroethane. [d] K_A not available. [e] 1,1,2,2-Tetrachloroethane.

Table 6. A comparison between the corrected second order rate constants for X⁻ +MeI→MeX+I⁻ in various solvents at 25.0 °C. (X=NCS⁻ and Cl⁻).

Solvent [a]	X=NCS⁻ $k_2(M^{-1}s^{-1})$	X=Cl⁻ $k_2(M^{-1}s^{-1})$
H₂O	3.16×10^{-4}	3.54×10^{-6}
MeOH	5.01×10^{-4}	3.16×10^{-6}
Formamide	1.58×10^{-3}	5.01×10^{-5}
DMF	7.9×10^{-2}	2.51
DMA	1.6×10^{-1}	7.9
MeCN	1.2×10^{-2}	1.2×10^{-1}
N-MePy [b]	1.58	25.1
Acetone	1.6×10^{-2}	5.01
CH₃NO₂	1×10^{-2}	5×10^{-2}
CH₂Cl₂ [c]	2.3×10^{-1}	5.6×10^{-1}

[a] From the survey in Ref. 14. [b] N-MePy is N-methylpyrrolidone. [c] This study.

methyl iodide as compared with the free thiocyanate ions since Bu₄NSCN is significantly more associated than are Ph₄AsSCN and [PNP]SCN, *cf.* Table 1.

The uncorrected rate constants for the MeI-NCS⁻ reaction in 1,2-dichloroethane and in 1,1,2,2-tetrachloroethane are slightly lower than in dichloromethane. The present lack of association constants for [PNP]SCN in these two solvents prevents the calculation of the corrected second order rate constants. However, the slight differences in the uncorrected rate constants may suggest that these solvents are equally valuable as solvents for organic substitution reactions.

In Table 6 a comparison is made between the corrected second order rate constants for the MeI-NCS⁻ and the MeI-Cl⁻ reactions in several protic and aprotic solvents including dichloromethane at 25.0 °C. In the case of Finkelstein reactions dichloromethane appears to be a significantly better solvent than are all the protic solvents and is actually comparable with the usual dipolar aprotic solvents. A similar observation has recently been made for a Menschutkin reaction, the EtI-pyridine reaction.[39] Apparently, rates of this type of substitution reactions are poorly correlated with the dielectric constant of the solvents.[56,57] The lack of any reliable correlation between the dielectric constant of the solvent and reaction rates was actually suggested by Hinshelwood nearly 50 years ago.[58]

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