Kinetic and Stereochemical Evidence for Nucleophilic Assistance in the Nucleophilic Hydrolysis of Chlorosilanes

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Summary Kinetic studies of the hydrolysis of chlorosilanes shows nucleophilic assistance by hexamethylphosphoric triamide, dimethyl sulphoxide, or dimethylformamide in nucleophilic substitution; the reaction is controlled by the entropy of activation, and takes place with retention of configuration at silicon instead of inversion as previous observed with acyclic chlorosilanes.

The activation of nucleophilic substitution at silicon has been reported;[1-5] this activation could be due either to

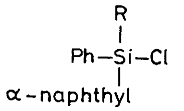
TABLE. Hydrolysis in anisole of triphenylchlorosilane (**1**), methyl-(α-naphthyl)phenylchlorosilane (**2**), and menthyloxy-(α-naphthyl)phenylchlorosilane (**3**) in the presence of the nucleophiles HMPT, DMSO, or DMF.[a]

Compound	Nucleophile	$k_3/l^2\ mol^{-2}\ s^{-1}$	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal $K^{-1}\ mol^{-1}$
(**1**)	HMPT	1200 ± 100	$-3{\cdot}4$	-56
(**1**)	DMSO	50 ± 10		
(**1**)	DMF	5 ± 1		
(**2**)	HMPT	3500 ± 400		
(**2**)	DMSO	180 ± 20	$1{\cdot}4$	-43
(**2**)	DMF	40 ± 5	$2{\cdot}6$	-40
(**3**)	HMPT	220 ± 20	$-2{\cdot}9$	-46

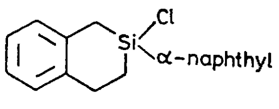
[a] The rate law $V = k_3[R_3SiCl][nucleophile][H_2O]$ was observed in all cases. The order of the hydrolysis with respect to the nucleophilic reagent was determined from the slopes of the curves $\log V_0 = f \log C_0$, where V_0 is the initial rate and C_0 the initial concentration of nucleophile, all other concentrations remaining constant. With excess of Ph_3SiCl and nucleophile the rate law was pseudo-first-order in H_2O. Plots of $\log[i^{\infty}_{HCl}/i^{\infty}_{HCl} - i^{t}_{HCl}]$ against time t are straight lines and their slopes k_1 are linearly dependent on the initial concentration of nucleophile and chlorosilane. Thus k_3 is given by $k_1/([R_3SiCl][nucleophile])$. The k_3 values are the average of 10 values with various concentrations of reactants.

coordination at silicon[2,5] or to an increase in nucleophilicity of the reagent.[4,5]

We describe now the dramatic change due to the presence of the nucleophilic agent hexamethylphosphoric triamide (HMPT) during hydrolysis of Si–Cl bonds. Substitution which does not take place in the presence of a small amount of water alone does occur, and the stereochemistry of the process changes from inversion to retention.



(**2**) R = Me
(**4**) R = Ph
(**5**) R = $CH_2{=}CH$



(**6**)

We have performed kinetic studies of the hydrolysis of chlorosilanes with a very low concentration of water (2×10^{-3} M) in an inert solvent (anisole).

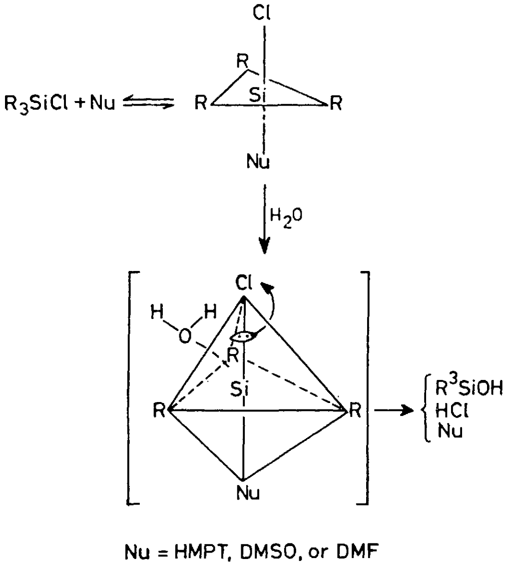
The kinetics were followed by amperometry at $-2{\cdot}5$ V (*vs.* Ag/Ag^+). HCl and Ph_3SiCl show two cathodic waves respectively at $E_{1/2}$ $-2{\cdot}1$ and $-3{\cdot}25$ V (*vs.* Ag/Ag^+) with anisole as solvent and $Bu^n_4NClO_4$ ($0{\cdot}2$ M) as supporting electrolyte.[6]

Without a nucleophilic reagent, no reaction occurs between the chlorosilane and the small amount of water included in the solvent. However, when HMPT ($0{\cdot}3$—14×10^{-3}M), dimethylformamide (DMF) (3—32×10^{-3}M), or dimethyl sulphoxide (DMSO) ($1{\cdot}7$—14×10^{-3}M) is added, hydrolysis does take place and HCl is produced. The current (i_D) is proportional to the amount of HCl produced. The results obtained are presented in the Table.

To obtain more information about the interaction between the nucleophilic agent and silicon, we have studied the stereochemistry of hydrolysis and methanolysis in presence of HMPT for the chlorosilanes (**2**), (**4**)—(**6**).

We observed a complete change in the stereochemistry of the hydrolysis: retention at silicon is observed instead of the inversion which is known to occur without nucleophilic agent.[7] The variation with time of the optical rotation at 365 nm showed symmetrical curves when the reaction (hydrolysis of alcoholysis) was performed in the presence or in the absence of HMPT. This provides the first example of retention of configuration at silicon in solvolysis of an acyclic chlorosilane.

The experimental facts are in good agreement with the hydrolysis being a nucleophile-assisted process involving co-ordination of the nucleophile at silicon. We propose that the first step is an expansion of the co-ordination at silicon, the rate-determining step being nucleophilic attack of water (Scheme).



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