Stereochemistry and Kinetics of a Chloride Exchange at Silicon

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Summary The chloride exchange reaction between Et_4NCl and $Me(ClCH_2)Si(Cl)NMe_2$ in CH_2Cl_2 solution proceeds with inversion and is first order in each component; the reaction was followed by an n.m.r. technique.

THE rates of chloride ion exchange in labile silicon–chlorine compounds have previously been studied by following the racemization of optically active silicon compounds[1] or by fast-reaction techniques involving tracers.[2,3] The reaction has been inferred to take place with inversion of configuration from the racemization experiments.[1,3] We now report a novel method for studying such reactions which, for suitable substrates, gives both stereochemical and kinetic information.

In the compound $Me(ClCH_2)Si(Cl)NMe_2$ the chloromethyl protons are diastereotopic[4] and give rise, in its ^1H n.m.r. spectrum in CH_2Cl_2 solution, to an AB quartet, J_{AB} 14·1 Hz. When a solution of Et_4NCl in CH_2Cl_2 is added, the AB spectrum collapses to an A_2 spectrum. By adjusting concentrations of the silicon compound, and of the salt, and by varying the temperature, partially collapsed n.m.r. spectra can be obtained and from these the rates of the chloride ion exchange can be obtained by line-shape analyses.[5]

The collapse of the AB spectrum to an A_2 spectrum is consistent with the exchange reaction proceeding with *inversion* of configuration at silicon, thus interchanging the magnetic environments of the diastereotopic protons of the chloromethyl group. We have previously made similar qualitative (but not quantitative) observations of chloride exchange with inversion in such labile 3-co-ordinate phosphorus compounds as $ClCH_2P(Cl)NMe_2$[6] and $CHCl_2CF_2$-$P(Cl)NMe_2$.[7]

Because line-shape analysis is not a very precise way of determining reaction rates, and because of the limited temperature ranges over which partially collapsed spectra can be observed, our kinetic conclusions are not yet as definitive as we would like. However for solutions at 80 °C, ranging from 0·019 to 0·038M in salt, and 0·85 to 1·52M in silicon compound, the reaction is approximately first order in each component. The Arrhenius activation energy for the reaction in these solutions over the temperature range of 70—95 °C is *ca.*† 4 kcal mol^{-1}.

There have been no previous kinetic studies of chloride exchange in analogous highly labile systems, but there have been studies on less labile compounds of the type R_3SiCl by fast reaction techniques.[3] These studies indicate that in acetone–dioxan as solvent reaction proceeded with inversion and was generally first order in silicon compound. The reaction was also first order in salt (LiCl) for some of the more reactive silicon compounds studied but was of lower order (*ca.* 0·5) for other compounds, and this was interpreted in terms of ion-pair equilibra. In CH_2Cl_2 (ϵ 9·1) Et_4NCl would be expected to be almost exclusively present as ion-pairs (or higher aggregates)[8] and the present results suggest that with our highly labile substrate, ion-pairs are kinetically fully active. The very low activation energy determined for our system is similar to those previously determined for R_3SiCl compounds.[3]

The present n.m.r. method of determining exchange rates of highly labile chloro-compounds may be a useful complement to existing methods.[1-3] It has the advantage of using starting materials which are relatively easy to prepare[4,9] and could be applied to a wide variety of systems in which diastereotopic groups are attached to a labile reaction centre. It suffers from the disadvantage of giving kinetic data which are not as precise as those obtained by more standard methods.

This work was supported by a Public Health Service Research grant from the National Cancer Institute. We thank Dr. S. Chan and Miss F. Fong for assistance in the preliminary stages of the work.

(*Received, 21st August* 1972; *Com.* 1461.)

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† The narrow temperature range available, and the difficulties of line-shape analysis,[5] make this value only a first approximation to be refined in future work.

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