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REACTIONS OF SUBSTITUTED SILYL RADICALS WITH CHLOROALKANES

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INTRODUCTION

The abstraction of chlorine atoms by silyl radicals, *in situ*, during a free radical addition reaction was reported by Haszeldine and Young[1]. A free radical mechanism was proposed for the reaction. This has been confirmed by later workers, and it has been shown, for the photochemical reaction of alkyl chlorides with trichlorosilane, that the ease of halogen abstraction decreases in the order tertiary > secondary > primary (C–Cl) bonds as expected from consideration of relative carbon–chlorine bond energies[2]. Halogen atoms and methyl radicals have been shown to have different selectivities[3,4] for the abstraction of hydrogen in different environments. The general pattern is that the more reactive a particular radical, the less selective it is in the abstraction reaction.

We describe below the effect of varying the silyl radical substituents on the selectivity of the silyl radical in chlorine abstraction.

RESULTS AND DISCUSSION

Photochemical reaction of the silanes $Me_nCl_{3-n}SiH$ ($n = 0$–3) with n-chlorohexane and with chlorocyclohexane in the liquid phase at 25° occurs according to the following equation:

$$X_3SiH + RCl \rightarrow X_3SiCl + RH$$

Irradiation of the chloroalkanes under the same conditions gave a trace of hydrogen chloride (0.5 %) and a little high boiling polymer. Irradiation of the silanes alone for the same time gave, for the chlorosilanes hydrogen (*ca.* 1 %) and hydrogen chloride (*ca.* 1 %), and for trimethylsilane using mercury photosensitisation, hydrogen (*ca.* 6 %). Abstraction reactions using trimethylsilane without added mercury were extremely slow (4 % after 100 h irradiation), consequently mercury photosensitisation was used in the abstraction reactions of trimethylsilane under discussion. The use of mercury photosensitisation in the photochemical decomposition of silanes has been previously discussed[5,6].

It has been previously suggested that the halogen abstraction reaction proceeds

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via a chain mechanism[1] and it has been shown that reaction (2) is rate determining for simple alkyl chlorides[2].

$$X_3SiH + h\nu \rightarrow X_3Si^{\bullet} + H^{\bullet} \tag{1}$$

$$X_3Si^{\bullet} + RCl \rightarrow X_3SiCl + R^{\bullet} \tag{2}$$

$$R^{\bullet} + X_3SiH \rightarrow RH + X_3Si^{\bullet} \tag{3}$$

Competition reactions of two different alkyl chlorides for the silyl radical can be used to investigate the selectivity of the radical for chlorine atoms in different environments. However, as the silanes are expected to have different chain transfer coefficients[7] and different quantum yields for equation (1), a similar competition of two silanes for one alkyl halide would not give meaningful results. The reactions reported here were carried out by competing each silane individually with the same pair of chloroalkanes in the presence of an inert reference material. Thus a comparison of the rate constant ratios for reaction (2) for each substituted silyl radical was made.

Mixtures of n-chlorohexane (R'Cl) and chlorocyclohexane (RCl) were photolysed in the presence of a 5:1 molar excess of the substituted silane and an inert reference of cycloheptane at 25°. The reaction of the chloroalkanes was followed with time by means of gas chromatography, hence the ration $k_2(RCl)/k_2(R'Cl)$ was obtained at various times throughout the reaction. The ratio $k_2(RCl)/k_2(R'Cl)$ was found to be independent of the initial concentration ratios $[RCl]/[R'Cl]$ over a range of ratios between 0.5 and 5, and independent of the time of the reaction up to 50% reaction of the minor reactant halide. The ratios are presented in Table 1 along with the percentage reaction of n-chlorohexane after 25 hours irradiation.

TABLE 1

SELECTIVITY OF THE METHYLCHLOROSILANES $Me_nCl_{3-n}SiH$ ($n = 0$–3) FOR CHLORINE ATOMS IN THE PHOTOCHEMICAL REACTION WITH CHLOROCYCLOHEXANE (RCl) AND n-CHLOROHEXANE (R'Cl) AT 25°

	Cl_3SiH	$MeCl_2SiH$	Me_2ClSiH	Me_3SiH	Me_3SiH[a]
$k_2(RCl)/k_2(R'Cl)$	5.64	3.04	2.46		1.84
% reaction of R'Cl after 25 h	26	52	15	0.5	7

[a] Mercury photosensitisation used.

It can be seen that abstraction occurs more readily with the secondary rather than the primary chlorine atom as expected. The selectivity of the silyl radical decreases with progressive substitution of methyl groups for chlorine. This can be interpreted as a progressive reduction in the reactivity of the silyl radicals, $Me_3Si^{\bullet} > Me_2ClSi^{\bullet} > MeCl_2Si^{\bullet} > Cl_3Si^{\bullet}$. Trimethylsilyl radicals seem to be the most reactive radicals of the series, although trimethylsilane is not necessarily the most reactive silane. Consistently the activation energies for hydrogen abstraction by methyl radicals for the compounds Me_3SiH, $MeCl_2SiH$, Cl_3SiH and F_3SiH[8] increase with increasing electronegativities of the substituents. The low percentage reaction for trimethylsilane may be due to a poor absorption of the radiation and an inefficient reaction (1).

The results indicate a decrease in the stability of the radical with increasing methyl substitution. The unpaired electron in the substituted silyl radicals will be in an antibonding orbital (classified as $6a^1$ for a tetra-atomic radical with C_{3v} symmetry)[9]. Electron-withdrawing groups polarise the bonding electrons in the direction of electron withdrawal, so that the antibonding orbitals are polarised away from the electronegative substituents. The unpaired electron thus becomes more localised at the central atom with increasing electron withdrawal from the atom*. If the stability of a radical is determined by the degree of delocalisation the predicted order of decreasing stability, $Me_3Si^\cdot > Me_2ClSi^\cdot > MeCl_2Si^\cdot > Cl_3Si^\cdot$ is the reverse of that observed. Both silicon and chlorine have *d*-type orbitals of relatively low energy. The inclusion of *d*-orbitals in forming the MO's for the silyl radicals would be expected to lower the energy which the 25th electron (the unpaired electron) will occupy. In valence bond language this is contributions from structures such as $X_2Si^+{-}Cl^-$. As the steric requirements of chlorine and methyl groups are similar it is suggested that *d*-orbital contributions may give rise to increasing delocalisation with increasing chlorine substitution and hence may account for the observed reactivity order.

EXPERIMENTAL

Photolyses were carried out both in sealed quartz tubes and in cylindrical quartz tubes fitted with shielded serum caps. For reactions with trimethylsilane sealed tubes only were used and the tubes were gently agitated. Irradiation was by a 250 watt Hannovia medium pressure mercury lamp. The tubes were placed 15 cm from the lamp and the liquid phase only was irradiated. For the reactions carried out in serum capped tubes sampling was by means of a hypodermic syringe. Identical reactions carried out in sealed tubes gave essentially the same results. For the reactions using trimethylsilane the tubes were cooled to -63° prior to sampling. Analysis was by gas chromatography using coupled Perkin–Elmer "A" and "C" columns (4 m) calibrated for the reactants. A standard of cycloheptane was used to determine the percentage reaction of the chloroalkanes. A 5 : 1 molar excess of the silanes was used. The purity of the reactants was checked before use by gas chromatography.

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SUMMARY

The photochemical reaction of the substituted silanes $Me_nCl_{3-n}SiH$ ($n = 0$–3) with a mixture of n-chlorohexane and chlorocyclohexane has been studied. The order of decreasing selectivity (and increasing reactivity) was found to be $Cl_3Si^\cdot > MeCl_2Si^\cdot > Me_2ClSi^\cdot > Me_3Si^\cdot$. A simple approach to the effect of substituents on a free radical predicts the reverse order of stabilities. Contribution to the bonding of the radicals from *d*-orbitals is invoked to explain the observed order.

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* The validity of this approach for simple tetraatomic radicals in which bonding involves only *s* and *p* type orbitals may be seen from the observation that $PO_3^\cdot$ and $SO_3^\cdot$ react with $H^\cdot$ to give HPO_3 and $HOSO_2$ respectively.

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