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Preliminary communication

Chlorine-abstraction and chlorine-migration reactions of silyl radicals

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We report preliminary experiments on some gas-phase reactions of silyl radicals, in which rapid chlorine-abstraction from silicon and a novel 1,2-chlorine shift, were observed. The silyl radicals were generated by hydrogen abstraction from organosilicon hydrides, using methyl radicals formed by thermolysis of either di-t-butyl peroxide in experiments up to 500 K, or dimethylmercury above 500 K; products were collected and analysed by MS 9 mass spectrometer.

$Me_2\dot{Si}Cl$ and $Me\dot{Si}Cl_2$ radicals were generated separately, from their respective hydrides, between 430 and 490 K; analogous products were formed in each case and the two reaction systems may be considered together, using the general formula $RMe\dot{Si}Cl$ (R = Me or Cl) for the radicals. The most prominent products were $RMeSiCl_2$ and $(RMeSiH)_2$, with smaller quantities of $RMeSiH_2$. No $(RMeSiCl)_2$ was observed. These findings are consistent with the following scheme:

$$RMeSiHCl + Me\cdot \longrightarrow RMe\dot{Si}Cl + CH_4 \qquad (1)$$

$$RMe\dot{Si}Cl + RMeSiHCl \longrightarrow RMeSiCl_2 + RMe\dot{Si}H \qquad (2)$$

$$RMe\dot{Si}H + RMeSiHCl \longrightarrow RMeSiH_2 + RMe\dot{Si}Cl \qquad (3)$$

$$2(RMe\dot{Si}H) \longrightarrow (RMeSiH)_2 \qquad (4)$$

Reaction (1) is well known to be rapid and exothermic, because silicon-hydrogen bonds are weaker than carbon-hydrogen. Since no $(RMeSiCl)_2$ was observed, we conclude that the transfer reaction (2), in which $RMe\dot{Si}Cl$ radicals are converted into $RMe\dot{Si}H$ radicals, is also rapid. The formation of $(RMeSiH)_2$ and of relatively small amounts of $RMeSiH_2$ implies that reaction (3) is considerably slower.

Chlorine-abstraction by silyl radicals from carbon-chlorine bonds is exothermic by at least 20 kcal, the minimum difference between the strengths of silicon-chlorine and carbon-chlorine bonds[1], and this type of reaction has recently been shown to be faster than addition of silyl radicals to the oxygen of halogeno-ketones and esters.[2] Our results show that chlorine abstraction by silyl radicals from silicon-chlorine bonds is also rapid, although there is now no substantial thermodynamic driving force, and indeed the bonds broken and formed in reaction (2) are considerably stronger than those in (3). The probable explanation for the greater rate of reaction (2) compared to reaction (3) lies in the possibility of *p–d* interaction between the chlorine of RMeSiHCl and the silicon of the incoming silyl radical, leading to stabilisation of the transition state for reaction (2).

Similar experiments were undertaken with $\mathrm{ClCH_2SiHMe_2}$ in the expectation that $\mathrm{\cdot CH_2SiHMe_2}$ radicals would be generated thus:

$$\mathrm{ClCH_2SiHMe_2 + Me\cdot \longrightarrow ClCH_2\dot{S}iMe_2 + CH_4} \qquad (5)$$

$$\mathrm{ClCH_2\dot{S}iMe_2 + ClCH_2SiHMe_2 \longrightarrow ClCH_2SiClMe_2 + \cdot CH_2SiHMe_2} \qquad (6)$$

However, there were no products attributable to $\mathrm{\cdot CH_2SiHMe_2}$ radicals, nor was any $\mathrm{ClCH_2SiClMe_2}$ observed, even up to 739 K. The only major product was trimethylchlorosilane, and we propose the following radical chain sequence:

$$\mathrm{ClCH_2SiHMe_2 + Me\cdot \longrightarrow ClCH_2\dot{S}iMe_2 + CH_4} \qquad (5)$$

$$\mathrm{ClCH_2\dot{S}iMe_2 \longrightarrow \cdot CH_2SiMe_2Cl} \qquad (7)$$

$$\mathrm{\cdot CH_2SiMe_2Cl + ClCH_2SiHMe_2 \longrightarrow Me_3SiCl + ClCH_2\dot{S}iMe_2} \qquad (8)$$

The rapid chlorine-migration reaction (7) is novel and interesting; 1,2-shifts in radicals are subject to orbital symmetry restrictions, but are allowed if the migrating group contains a second-row element with vacant *d*-orbitals. Thus, migration of silyl groups in organosilicon radicals has been observed, *e.g.*[3] $\mathrm{Me_3SiSiMe_2\dot{C}H_2 \rightarrow Me_2\dot{S}iCH_2SiMe_3}$; and 1,2-shifts of chlorine in alkyl radicals are well known,[4] including $\mathrm{Me_2ClC\dot{C}H_2 \rightarrow Me_2\dot{C}CH_2Cl}$. Reaction (7) appears to be unconventional in that a tertiary radical is converted into a primary radical, the opposite trend being followed in rearrangements of alkyl radicals due to the relatively greater strength of bonds to primary carbon atoms. However, reaction (7) occurs because of the substantially greater strength of the silicon-chlorine bond compared to carbon-chlorine.

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