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Preliminary communication

Gas-phase reactions of silicon-centred intermediates with chlorofluorocarbons [1]

Michael P. Clarke, Martin Conqueror, Geraint H. Morgan, Iain M.T. Davidson *

Department of Chemistry, The University, Leicester LE1 7RH, UK

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Abstract

Pyrolysis of pentamethyldisilane in the presence of a CFC, dichlorodifluoromethane, efficiently replaced chlorine by hydrogen in the CFC, with concomitant formation of chlorosilanes. Although the primary intermediate in this pyrolysis is dimethylsilylene, there was strong evidence that conversions resulted from reactions of organosilyl and alkyl radicals. Experiments to confirm this conclusion are described, and mechanisms are discussed. Two independent measurements of the activation energy difference between chlorine- and fluorine-abstraction from dichlorodifluoromethane by trimethylsilyl radicals gave concordant values of 52 ± 5 kJ mol^{-1}. The reactions described are of interest in relation to the environmental importance of dechlorinating CFCs.

Keywords: Pyrolysis; Chlorofluorocarbons; Kinetics; Silylene; Silyl; Radical

1. Introduction

In the course of a study of the role of silylenes in the Direct Synthesis [1], we had occasion to investigate the reaction of silylenes with chlorofluorocarbons (CFCs). The well known propensity of silicon-centred intermediates to abstract chlorine from chloromethane and other alkyl chlorides prompted us to wonder whether such intermediates could dechlorinate CFCs. Dechlorination of CFCs is, of course, of considerable interest in view of the environmental implications of the threat to the ozone layer caused by solar photodissociation in the stratosphere of the carbon–chlorine bond in CFCs.

2. Experimental

Pyrolysis experiments were carried out in a batch stirred-flow apparatus, as described previously [2], with analysis by GLC/mass spectrometry (HP5995C). Mercury-photosensitisation experiments were conducted in a quartz cell mounted in a heating block and irradiated by a mercury 254 low-pressure lamp.

3. Results and discussion

1 : 1 mixtures of $Me_3SiSiMe_2H$ and CF_2Cl_2 were pyrolysed in a stirred flow apparatus between 710 and 766 K, at partial pressures between 1.5 and 3 mm Hg. The main products revealed by GLC-MS analysis fell into three groups: the most abundant were $Me_3SiSiMe_2Cl$ and Me_3SiCl; in the second, less abundant, group were Me_2SiCl_2 and Me_3SiH, which formed in amounts similar to the amount of $Me_3SiSiMe_2H$ remaining; the third, least abundant, of the main products was HCF_2Cl, the amount of which approximately equalled the amount of undecomposed CF_2Cl_2. In addition, there were several minor products, including $(CF_2Cl)_2$, CF_2ClCF_2H and, at higher temperature, Me_3SiF.

The extent of the decomposition of $Me_3SiSiMe_2H$ in these experiments was significantly greater than would be expected from the well-established kinetic parameters [3] for the unimolecular elimination of dimethylsilylene, $:SiMe_2$, suggesting the occurrence of a chain sequence. The formation of $Me_3SiSiMe_2Cl$, Me_3SiCl, HCF_2Cl, $(CF_2Cl)_2$, CF_2ClCF_2H and Me_3SiF strongly indicate that the main intermediates in this sequence are radicals, not silylenes.

These observations may be explained by the reaction sequence in Scheme 1, in which reactions (2) and (5) are of central importance. Thermally-produced silylenes, being in the singlet state, would not normally be ex-

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* Corresponding author.

[1] Dedicated to Professor Robert Corriu, an outstanding and stimulating organosilicon chemist.

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$Me_3SiSiMe_2H \rightarrow Me_2Si: + Me_3SiH$ (1)

$Me_2Si: + CF_2Cl_2 \rightarrow [Me_2Si\text{--}Cl\text{--}CF_2Cl]$

$\rightarrow Me_2Si(Cl). + .CF_2Cl$ (2)

$.CF_2Cl + Me_3SiSiMe_2H \rightarrow HCF_2Cl + Me_3SiSi(Me_2).$ (3)

$Me_3SiSi(Me_2). + CF_2Cl_2 \rightarrow .CF_2Cl + Me_3SiSiMe_2Cl$ (4)

$Me_3SiSi(Me_2). \rightarrow Me_3Si. + Me_2Si:$ (5)

$Me_3Si. + CF_2Cl_2 \rightarrow Me_3SiCl + .CF_2Cl$ (6)

$Me_2Si(Cl). + CF_2Cl_2 \rightarrow Me_2SiCl_2 + .CF_2Cl$ (7)

$.CF_2Cl + Me_3SiH \rightarrow HCF_2Cl + Me_3Si.$ (8)

(followed by radical combination reactions forming $(CF_2Cl)_2$ and CF_2ClCF_2H)

Scheme 1.

pected to undergo abstraction reactions. However, they can form adducts to electronegative atoms with lone pairs [4], such as chlorine, which in this case would then dissociate at the weakest bond, as shown in reaction (2), to form silicon-centred and carbon-centred radicals.

In the temperature range of these experiments, reaction (5) would be rapid. The kinetics of the corresponding dissociation of the silicon–silicon bond in hexamethyldisilane are well established [5], with $\log A$ $(s^{-1}) = 17.2$ and $E = 337$ kJ mol^{-1}. Reaction (5) would have a similar A factor, while the activation energy would be reduced by the silylene stabilisation energy [6] from 337 to 219 kJ mol^{-1}, giving a half-life of 0.03 s at 723 K. Reaction (5) not only propagates the chain, but accounts for the striking fact that approximately equal amounts of Me_3SiCl and $Me_3SiSiMe_2Cl$ were formed.

At the higher end of the temperature range, some Me_3SiF was observed, presumably formed by reaction (9).

$Me_3Si. + CF_2Cl_2 \rightarrow Me_3SiF + .CF_2Cl$ (9)

The activation energy difference between reactions (6) and (9) was estimated in a separate series of experiments between 758 and 900 K, in which the peak areas of Me_3SiF and Me_3SiCl were measured. An Arrhenius-type plot of the ratio of these areas gave $(E_9 - E_6) = 52 \pm 5$ kJ mol^{-1}.

In view of the strong evidence for the participation of $Me_3Si.$ radicals, some experiments were done in which $Me_3Si.$ radicals were generated in the presence of CF_2Cl_2. Mercury photosensitisation of Me_3SiH was used as the source of $Me_3Si.$ radicals [7], with photolysis times ranging from 5 to 90 min.

At 298 K, the main product was Me_3SiCl, followed by HCF_2Cl; the only other significant products were $(CF_2Cl)_2$ and CF_2ClCF_2H. At 603 K, the same products were formed, together with CF_2CH_2 and Me_3SiF.

Formation of all of these products may be explained in terms of reactions (6), (8), (9) and the radical combination reactions in Scheme 1, with the CF_2CH_2 being produced as a result of HCF_2Cl undergoing analogous chlorine- and hydrogen-abstraction reactions to (6) and (8).

The activation energy difference between fluorine- and chlorine-abstraction from CF_2Cl_2 by $Me_3Si.$ radicals, $(E_9 - E_6)$, was measured in a similar way to the thermal experiments. As the $Me_3Si.$ radicals were produced photochemically, the temperature range was much lower, 427 to 463 K. The result was 52.5 ± 5.5 kJ mol^{-1}, in excellent agreement with the thermal experiments between 758 and 900 K. As the activation energy for chlorine-abstraction from MeCl by $Me_3Si.$ radicals is 17 kJ mol^{-1} [8], we estimate $E_9 \approx 70$ kJ mol^{-1}.

4. Conclusions

Silicon-centred intermediates are capable of bringing about the following metathesis reactions, thus dechlorinating CFCs:

$$\equiv SiH + CF_2Cl_2 \rightarrow \equiv SiCl + HCF_2Cl$$

$$\equiv SiH + HCF_2Cl \rightarrow \equiv SiCl + CF_2H_2$$

The radical chain sequence by which dechlorination occurs may be initiated by silyl radicals or by silylenes, which generate silicon-centred and carbon-centred radicals through the intermediacy of a donor–acceptor adduct.

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