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CALCULATION OF ACTIVATION ENERGIES IN THE CHLORINATION OF DISILANE

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Summary

Activation energies have been calculated for the bimolecular reactions

$Cl_2 + Si_2H_6 \rightarrow 2ClSiH_3$ $E_{act} = 31.5$ kJ mol^{-1}

$Cl + Si_2H_6 \rightarrow ClSiH_3 + SiH_3$ $E_{act} = 6.7$ kJ mol^{-1}

and the results used to comment on the mechanism proposed for the chlorination of hexamethyldisilane.

Introduction

Mechanisms have recently been proposed [1] for the chlorination of tetramethylsilane and hexamethyldisilane (HMDS). Whereas the former is initiated by Cl atoms from the photolysis of chlorine, HMDS is chlorinated through a dark thermal reaction and initiation is proposed to be through the highly exothermic reaction

$$Cl_2 + Si_2Me_6 \rightarrow 2ClSiMe_3 \quad (1)$$

The complexities of the overall reaction precluded an estimate of the Arrhenius parameters from the experimental measurements. The problem is therefore now approached from a theoretical viewpoint. In order to make the problem calculationally tractable, the present work involving the calculation of activation energies was confined to the systems $Cl_2 + Si_2H_6$ and $Cl + Si_2H_6$. By analogy, these results are used to comment on previous mechanistic proposals for the $Cl_2 + Si_2Me_6$ and $Cl + Si_2Me_6$ systems.

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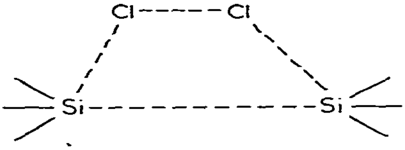
Method

The method used for calculating the activation energies for the reactions of interest was essentially the same as that previously employed for the chlorination of paraffin hydrocarbons [2,3]. In each case the heat of atomisation for the overall interacting system was computed in the standard state and at 298 K along the reaction coordinate (i.e., at various positions in the coordinate space) so that the minimum enthalpy path from reactants to products could be obtained.

We consider first the reaction between Cl_2 and Si_2H_6, i.e.:

$$Cl_2 + Si_2H_6 \rightarrow 2ClSiH_3 \qquad (2)$$

Reaction 2 is considered to occur through molecular interaction of Cl_2 across the Si—Si bond, giving rise to a symmetrical transition state, i.e.:



In our calculations, all the bond angles and Si—Si and Cl—Cl bond lengths were allowed to change concomitantly with the changing Si—Cl distance. This affords a single variable along the reaction coordinate. For each geometrical variation considered, a quantum-mechanical self-consistent field (CNDO-type [4]) calculation was performed. This yields a set of bond indices [5] which can be correlated directly with bond energies [2,3]. These calculations were used in conjunction with the bond-energy parameters derived from previous work [3,6] to obtain heats of atomisation for the points on the reaction coordinate. The bond energy parameters used in the present work are listed in Table 1. A survey of the heats of atomisation over the region of interest reveals the minimum enthalpy path for the reaction and, hence, the activation enthalpy, $\Delta H^{0\ddagger}$, for the reaction may be computed. Since the reaction is bimolecular, the energy of activation, E_{act}, is given by

$$E_{act} = \Delta H^{0\ddagger} + 2\,RT$$

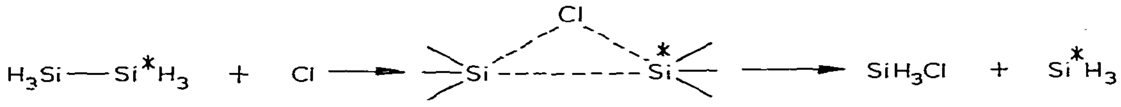
The reaction between Si_2H_6 and Cl atoms was studied in an analogous way.

TABLE I

BOND ENERGY PARAMETERS

Atom pair	Bond energy parameter ($kJ\ mol^{-1}$)
Si—Si	163.76
Si—H	322.33
Si—Cl	329.49
Cl—Cl	141.96
"non-bonded" Si—H	298.90
"non-bonded" Si—Cl	241.92
"non-bonded" H—Cl	25.86

Here the system studied was,



The calculations were performed such that as the Si—Cl bond becomes shorter then the Si—Si$^+$ bond lengthens and the hydrogen atoms around Si* assume a trigonal instead of a tetrahedral geometry. The enthalpy of activation is again obtained from a survey of the heats of atomisation in the appropriate region of coordinate space.

Results and discussion

From the computed enthalpy of activation corrected for temperature (400 K) an energy of activation of 31.5 kJ mol^{-1} was calculated for the initiating process (reaction 2).

Making the assumption that a similar activation energy would prevail for the reaction $Cl_2 + Si_2Me_6$ and assuming a value of 10^{12} ml mol^{-1} s^{-1} as a reasonable A factor for the bimolecular reaction, a value for $k_{\text{initiation}} = 8 \times 10^7$ ml mol^{-1} s^{-1} is obtained at 400 K.

This value is of a magnitude which would support the proposal that reaction 1 is sufficiently facile as to provide the dark thermal initiating step.

It was further proposed by Bell and Davidson [1] that, due to the high exothermicity of reaction 1, the product would be energy-rich, resulting in formation of Cl atoms and the setting up of a chlorination chain.

Use of our calculated [6] thermodynamic data allows us to compute a heat of reaction for reaction 1 of —348 kJ mol^{-1} which, assuming equipartition of energy, imparts an excess energy of 174 kJ mol^{-1} to each $ClSiMe_3$ molecule produced.

This would be insufficient to cause the dissociation of Cl_2 molecules directly, and thus reaction 3, proposed by Bell and Davidson [1], appears the most likely route to the formation of Cl atoms.

$$ClSiMe_3^* + Cl_2 \rightarrow Cl_2\text{—}SiMe_3^* + Cl \qquad (3)$$

The Cl atoms could then initiate a chain through reactions 4 and 5.

$$Cl + Si_2Me_6 \rightarrow ClSiMe_3 + SiMe_3 \qquad (4)$$

$$SiMe_3 + Cl_2 \rightarrow ClSiMe_3 + Cl \qquad (5)$$

Reaction 5 is expected to be rapid and we have calculated the energy of activation for $Si_2H_6 + Cl$ (cf. reaction 4) as 6.7 kJ mol^{-1}. By analogy, reaction 4 should also be facile.

We conclude that the mechanistic proposals made for the chlorination of HMDS [1] are reasonable on activation energy grounds.

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