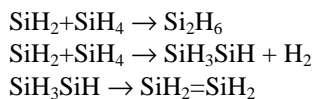


NON-EQUILIBRIUM EFFECTS DURING DISILANE DECOMPOSITION

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Kinetic data on the reactions of silylene radicals with silane have been analyzed using the rigorous master equation approach for the determination of the distribution functions. Non-thermal effects have been quantified. The following reactions have been considered.



The first two reactions are chemical activation process, while the third reaction is an isomerization involving an extremely small barrier. All of these processes are characterized by non-thermal distribution functions. Energy transfer effect can therefore be expected to have an important effect on the rate constants. These reactions are the processes that immediately follow the first step in gas phase silane pyrolysis. Indeed, they are probably important in any high energy system where silane is present.

Past work in this area have relied on various approximations that are now known to be invalid or with the increases in computational capability, need no longer be made. The aim of this work is to apply more modern understanding to the analysis of these reactions. The procedure involves first the development of a base of information for the analysis. This includes collecting information on the thermodynamic and kinetic properties of the systems. Particularly important are the high pressure rate expressions for the two channel decomposition of silane and the isomerization of silylsilene.

With this information, transition state frequencies and structures are developed. Note that for the present purposes the key requirement is that the high pressure rate expression be reproduced. These and the

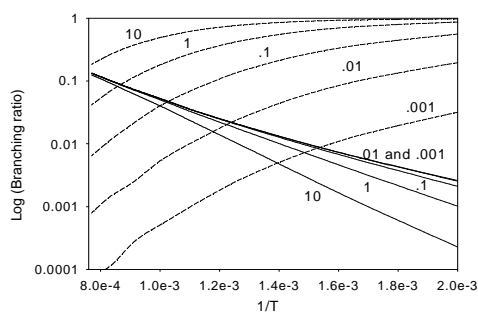


Figure 1: Branching ratios as a function of temperature. Solid line for silylsilene formation. Dotted line for disilane formation. Numbers are in bar

properties of the molecules are then used to solve for the distribution function of the decomposing molecule on the basis of the master equation approach. Convoluting the distribution function with the RRKM specific rates

yields time dependent rate constants.

Results for the chemically activated decomposition of disilane can be seen in Figure 1. Comparison with earlier work show fairly good agreement. It is suspected that this is largely due to the closeness of the values of the reaction barriers to each other and that the reactions are very near threshold. It is clear that in this case the uncertainties in the high pressure rate expressions for silylsilene formation is the most serious source of error.

In the case of the isomerization reaction the present analysis indicate that beginning at temperatures very close to ambient the steady state distributions necessary to determine constant rate constants are not achieved. Instead the rate constants decrease with extents of conversion. At the highest temperatures the high pressure rate constants are recovered. This can be seen in

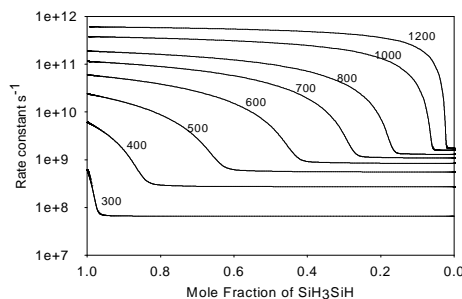


Figure 2: Rate constants for silylsilene isomerization as a function of time. The numbers refer to the temperature.

Figure 2. Thus standard treatments can well be underestimated. The consequences of such behavior may however not be serious in this case since it is a consequence of the large rate constant. If it is so large that no other process can compete than exact values are not require. It is probably more serious in multichannel reactions if accurate branching ratios are required.