Pressure-dependent Isotope Effect in the Reaction of Silylene (SiH_2, $^1A_1$) with Acetylene and [$^2H_2$]Acetylene

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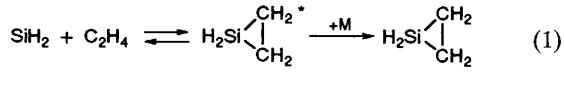
Direct, time resolved measurements of absolute rate constants for reaction of $SiH_2(^1A_1)$ with C_2H_2 and C_2D_2 have revealed a pressure (and temperature) dependent isotope effect characteristic of an association process yielding an intermediate (silirene) which undergoes, amongst other reactions, a degenerate isotopic scrambling process.

We have recently found,[1,2] by direct kinetic studies, that the reaction of $SiH_2(^1A_1)$ with C_2H_4 exhibits a pressure dependence characteristic of a third-body mediated association reaction, eqn. (1).



(1)

RRKM calculations show that the pressure dependence is consistent with formation of silirane with an excess of energy in agreement with predictions based on the most recent *ab initio* calculations[3,4] of its enthalpy of formation. The contrasting kinetic behaviour of $SiH_2(^1A_1)$ and $CH_2(^1A_1)$ were explained on energetic grounds. We describe here new results on the kinetics of the reaction of $SiH_2(^1A_1)$ with C_2H_2, which now enable us to compare and contrast the reactions of SiH_2 with the two different substrates, C_2H_2 and C_2H_4. In order to illuminate the mechanism of reaction further we have additionally carried out a gas-phase study of $SiH_2(^1A_1)$ with C_2D_2. The only existing rate datum for the $SiH_2 + C_2H_2$ reaction is that of Jasinski *et al.*[5] who obtained a value of 9.8×10^{-11} cm^3

molecule^{-1} s^{-1} for the rate constant at 298 K in the presence of He [total pressure, 5 Torr (1 Torr = 133.3 Pa)].

SiH_2 kinetic studies were carried out by the laser flash photolysis technique, details of which have been published previously.[6,7] SiH_2 was generated by photodecomposition of phenylsilane ($PhSiH_3$) using the 193 nm ArF line of a pulsed exciplex laser. SiH_2 was detected and monitored in real time by use of a single mode dye laser tuned to a known (strong) vibration–rotation transition (17259.50 cm^{-1}) in its visible $\tilde{A} \leftarrow \tilde{X}$ absorption band. Signal decays from 5 to 15 photolysis laser shots were averaged and found to give good first-order kinetic fits. The timescale (μs) of the transient decays, precludes migration of SiH_2 out of the reaction zone during experimental runs and thus ensures that these processes must be homogeneous and not surface mediated. Experiments were carried out with gas mixtures containing a few mTorr of $PhSiH_3$, varying quantities of C_2H_2 (or C_2D_2) up to 200 mTorr and SF_6 up to total pressures between 1 and 30 Torr. The acetylenes were gas chromatographically pure but the C_2D_2 contained a 20% impurity of C_2HD.

Second-order kinetics was confirmed by the linear dependence of the first-order decay constants on substrate C_2H_2 or C_2D_2 pressures at a total pressure of 10 Torr. The second-order rate constants from these experiments and those obtained at other pressures both at 291 and 613 K are given in Table 1. The error limits shown for the 10 Torr data are single standard deviations. For the other rate constants, based on less points, the uncertainties are *ca.* ± 10%. The values show (*i*) an isotope effect favouring reaction with C_2D_2, which varies with both pressure and temperature; (*ii*) a pressure dependence of the rate constants which is least marked for C_2D_2 at 291 K and most marked for C_2H_2 at 613 K; (*iii*) a decrease in rate constants with increasing temperature. A fuller set of experiments is being carried out[8] but the results obtained so far permit us to draw certain conclusions.

The observed pressure dependence for the $SiH_2 + C_2H_2$ reaction shows that the reaction has, at least in part, the characteristics of a third-body mediated association reaction. In this respect the reaction is similar to $SiH_2 + C_2H_4$ although the pressure dependence is less marked. Our results are consistent with those of Jasinski *et al.*,[5] after consideration of the much weaker collisional stabilising efficiency of the He bath gas used in their experiments. The very weak pressure dependence for $SiH_2 + C_2D_2$ suggests an association process in which re-elimination of SiH_2 from the incipient (collisionally unstabilised) adduct is at most a minor pathway. At high pressures the rate constants for both reactions approach one another in value (*i.e.* the isotope effect diminishes) consistent with convergence towards the true bimolecular addition rate constant (for which there should be only a small secondary isotope effect between the two systems). The low probability of re-elimination of SiH_2 in the $SiH_2 + C_2D_2$ reaction can be explained if the energised intermediate is capable of scrambling the isotopic label such that elimination of SiHD and SiD_2 become possible. If statistical scrambling is achieved then silylene elimination will correspond to 17% SiH_2, 17% SiD_2 and 66% SiHD. The data are consistent with nearly complete scrambling at room temperature but a lesser extent at 613 K.

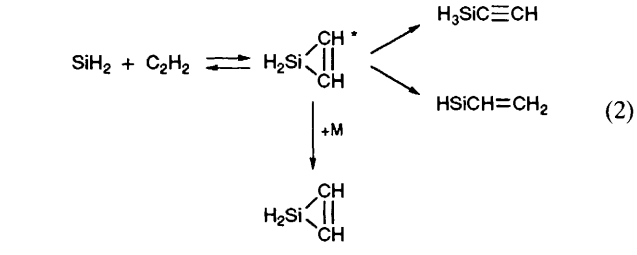
Table 1 Experimental rate constants for reaction of $SiH_2 + C_2H_2/C_2D_2$

	$k/10^{-10}$ cm^3 molecule^{-1} s^{-1}	
P/Torr	C_2H_2	C_2D_2
1.0[a]	1.80	2.73
3.0[a]	2.57	3.45
10.2[a]	3.54 ± 0.22	3.80 ± 0.14
31.4[a]	3.57	3.31
0.94[b]	0.202	0.607
3.1[b]	0.449	1.176
10.2[b]	0.716 ± 0.026	1.44 ± 0.06
31.7[b]	0.934	1.52

[a] T = 291 ± 3 K. [b] T = 613 ± 5 K.

In order to assess the pressure dependence in $SiH_2 + C_2H_2$ we have carried out an RRKM calculation based on the assumed formation of silirene. Since silirene is an experimentally unknown molecule no kinetic study of its decomposition exists. However, a reasonably reliable assignment of its transition state vibrations and structure can be obtained *via* the theoretically calculated geometry and vibration frequencies of silirene itself,[9] combined with an estimated *A* factor of $10^{16.8}$ s^{-1} for its decomposition to $SiH_2 + C_2H_2$. This *A* factor is calculated from the association *A* factor of $10^{-9.9}$ cm^3 molecule^{-1} s^{-1} obtained from our measurements, combined with a reaction entropy estimate based on a statistical-mechanical calculation.[8] Since the activation energy is experimentally unknown, four calculations were carried out at different energies. For these purposes a strong collisional deactivation model was used although it was verified that for a weak model corresponding to known efficiencies for SF_6 in other systems there were very little differences. Fig. 1 shows the results of these calculations compared with the measurements. Clearly the closest approximation to a fit corresponds to the highest activation energy of 268 kJ mol^{-1}. This is some 63 kJ mol^{-1} higher than the lowest value modelled, which, however, corresponds closely to the most recent theoretical estimate.[10] Since RRKM modelling was successful, with the theoretically based decomposition activation energy (for silirane) in the $SiH_2 + C_2H_4$ system,[1] an alternative explanation is offered for the $SiH_2 + C_2H_2$ reaction. If a fraction of the initially formed energized silirene isomerises into another product, then pressure quenching of the reaction will be less effective, and pressure dependence less marked.

These findings can be encapsulated in the following mechanism (hydrogenated system only), eqn. (2).



(2)

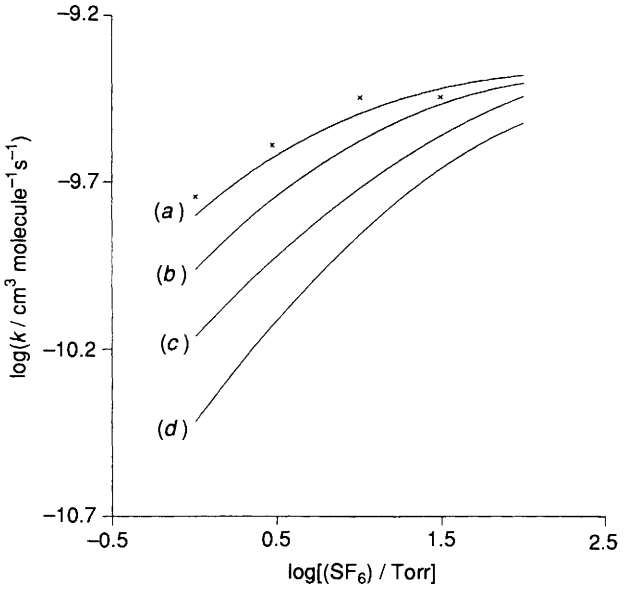


Fig. 1 Comparison of experiment, x, with RRKM theory calculated pressure-dependencies for $SiH_2 + C_2H_2$. Theoretical lines correspond to activation energies in kJ mol^{-1} for the silirene adduct decomposition of: (*a*) 268; (*b*) 247; (*c*) 226; (*d*) 205.

This mechanism has been previously suggested by O'Neal *et al.*[11] from high-temperature pyrolysis studies with end product analysis. Our direct kinetic measurements offer dramatic evidence for its occurrence down as low as room temperature. The most interesting feature of this mechanism is the facile reversible ring-opening reaction of silirene to vinylsilylene. The silirene ring shows more versatility in its chemistry than its all-carbon analogue, cyclopropene.

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