Silylene Does React with Carbon Monoxide

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Silylene, SiH_2, is known to react rapidly and efficiently with many chemical species.[1,2] Examples of its reactions include Si−H bond insertions, C═C and C≡C π-bond additions, and reactions with lone pair donors.[3] It therefore appears somewhat surprising that direct, time-resolved kinetic studies by Chu et al.[4] of the reaction of SiH_2 with CO give an upper limit for the reaction rate constant of only 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (in the gas phase in 5 Torr He buffer gas). This corresponds to a collision efficiency of less than 10^{-3}, and contrasts with the reaction of $^1CH_2 + CO$ which is at least 400 times faster. The stimulus for the present reinvestigation of this reaction was the recent report by Maier et al.[5] of the IR spectrum of silaketene, H_2SiCO (the probable product of $SiH_2 + CO$), in a frozen Ar matrix at 12 K. The study was supported by ab initio calculations[5] which suggest that H_2SiCO is slightly more stable than previously thought.[6] The story is somewhat paralleled by the situation in respect of the potential reaction between dimethylsilylene, $SiMe_2$, with CO where no gas-phase reaction could be found in our laboratory[7] while matrix isolation studies[8,9] strongly point to formation of Me_2SiCO.

We reasoned that a possible cause for the failure to find reaction in the earlier kinetic studies might have been the low pressures employed, allied with the inefficiency of helium as a collision partner. Thus the reaction might well initially form vibrationally excited silaketene as shown in the scheme, but which may rapidly redissociate via breaking of its weak bond unless collisionally stabilized. In other words this is potentially a classic example of an association reaction requiring a third body.

$$H_2Si + CO \rightleftarrows H_2SiCO^* \xrightarrow[M]{} H_2SiCO \qquad (1)$$

Thus our approach was to investigate the reaction at much higher pressures and with SF_6, a known efficient collision partner, as bath gas.

The gas-phase kinetic studies with SiH_2 were carried out by the laser flash photolysis technique, the details of which have been published previously.[10,11] SiH_2 was generated by photodecomposition of phenylsilane using the 193 nm ArF line of a pulsed excimer laser. SiH_2 concentrations were monitored in real time by means of a single-mode dye laser tuned to the known 17259.50 cm^{-1} ro-vibrational transition[12] in the visible A ← X absorption band. Signal decays from 5 to 20 photolysis laser shots were averaged and found to give good first-order kinetic fits. Experiments were carried out with gas mixtures containing a few mTorr of phenylsilane, varying quantities of CO (>99.96% pure) up to 10 Torr, and inert diluent SF_6 to total pressures between 10 and 500 Torr.

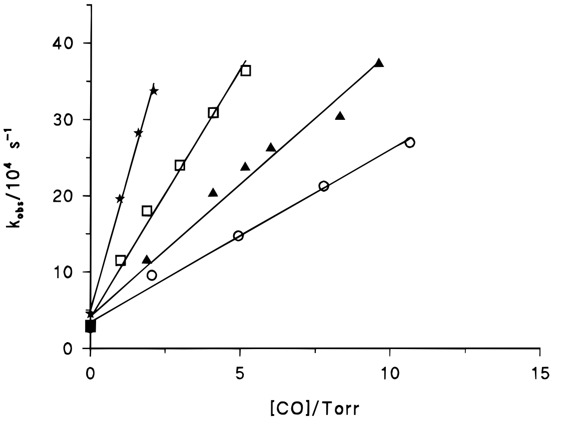

Figure 1. Some second-order plots of the dependence of k_{obs} on carbon monoxide pressure at different overall pressures/Torr (SF_6): ○, 30; ▲, 50; □, 100; *, 200.

Initial studies at 10 Torr total pressure with varying CO pressures up to 10 Torr showed a significant, although fairly small, effect of CO on the pseudo-first-order decay constants, k_{obs}, for SiH_2. However, at higher total pressures the effect of added CO was much larger. Some examples of these results are shown in Figure 1. The linear dependence of k_{obs} on [CO] indicates second-order behavior, consistent with the association reaction 1. The second-order plot gradients of Figure 1 and the rest of the data are themselves nearly linearly proportional to total pressure over the range 20−500 Torr. This indicates an overall third-order reaction consistent with a third body assisted association (combination) as surmised. The results give a third-order rate constant of $(6.9 \pm 0.8) \times 10^{-31}$ cm^6 $molecule^{-2}$ s^{-1}.

To gain further support for the suggested mechanism we have carried out RRKM calculations[13] based on the silaketene structure and vibrations found by Maier et al.[5] These calculations employed a loose transition state consistent with our findings for other silylene reactions of insertion[11] and addition,[14] and suggested by the experimental results obtained here, of a fairly fast reaction. The loose transition state vibrational assignment was obtained by reducing the wavenumbers of the transitional modes of the silaketene (SiH_2 wag and bend, Si−C≡O bends). The bond energy (RRKM critical energy) was varied within the range 90−121 kJ mol^{-1} (21.5−29.0 kcal mol^{-1}) corresponding to values found from the various different levels of ab initio calculation.[5] The collisional stabilization model (effectively the efficiency of SF_6) assumed an average removal of 12.0 kJ mol^{-1} in a down collision consistent with findings in similar reaction systems.[11,14] The key to fitting the results was to find the optimum parameters which corresponded to the third-order kinetic region (corresponding also to the low-pressure limit for dissociation of silaketene). A grid search gave the best fit for the loosest transition state tried, with

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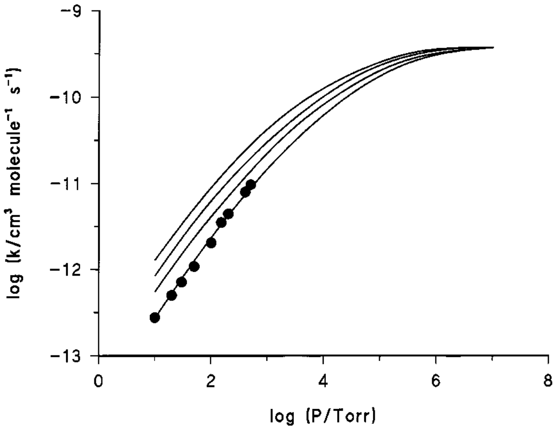

Figure 2. Pressure dependence of the second-order rate constants for reaction 1 at 299 K. The curves shown are derived from RRKM theory (see text) for different critical energies of 121, 111, 100, and 90 kJ mol^{-1} with the last giving the best fit.

$E_o = 90$ kJ mol^{-1} (21.5 kcal mol^{-1}). Some sample curves showing the pressure dependence of the second-order rate constant are shown in Figure 2. The optimal curve shows a close fit to the data and the family of curves show that the limiting (high pressure) second-order rate constant has a value of ca. 3.3×10^{-10} cm^3 molecule^{-1} s^{-1}. This corresponds to the collision rate for $SiH_2 + CO$! Although this figure is not established with the certainty of a direct measurement, nevertheless our calculations show that without a rate constant close to this value (within a factor of 2) the pressure-dependent “fall-off” effect cannot reach the third-order limit in our experimental range. Our measurements combined with the calculations confirm that under the conditions of the study by Chu et al.,[4] expected values for the rate constant would be below their threshold of measurement.

We are continuing our study of this reaction by extending measurements to higher temperatures to refine further the kinetic model of the process and the value for the binding energy of H_2SiCO. It is, however, already clear that silylene, rather than being unreactive with carbon monoxide, in fact reacts with it at almost every collision.

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