The Recombination Rate of Trimethylsilyl Radicals in the Gas Phase

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Summary The rate of recombination of trimethylsilyl radicals has been measured in the gas phase by a rotating sector technique and found to be $10^{14\cdot25\pm0\cdot3}$ cm^3 mol^{-1} s^{-1}.

THE reactions of free radicals containing the odd electron on a carbon atom are well catalogued.[1] The reactions of radicals where the unpaired electron is situated on an atom other than carbon have not been so thoroughly investigated.[1,2] The recombination of carbon radicals has been measured by various techniques both in solution[3] and in the gas phase,[4] but the only measurements of recombination of radicals of other Group IV elements have been those by Ingold and his co-workers[3,5] for solutions. Recently a value of the rate coefficient of recombination of trimethylsilyl radicals in solution was obtained by e.s.r. measurements.[5] We report a value for the coefficient of recombination of trimethylsilyl radicals in the gas phase. This is the first value for the rate of gas-phase recombination of radicals of a Group IV element other than carbon. This rate coefficient was found to be $10^{14\cdot25\pm0\cdot3}$ cm^3 mol^{-1} s^{-1} between 317—399K and was independent of temperature. This can be compared with the value[5] of $10^{12\cdot3}$ cm^3 mol^{-1} s^{-1} obtained at 298K for solutions. The rate coefficient in both the gas phases and in solution corresponds to recombination at nearly every collision.

The method used in this investigation was the classical rotating sector technique used previously to measure the rate of combination of carbon radicals.[4] The trimethylsilyl radicals were produced from trimethylsilane by mercury photosensitisation 253·7 nm in a short path-length cell. This method was found to be a good source[6] of trimethylsilyl radicals. The recombination of the trimethylsilyl radicals to form hexamethyldisilane (reaction 2) competed against the abstraction of chlorine from ethyl chloride (reaction 1) using both steady and intermittent light.

$$\mathrm{Me_3Si\cdot + EtCl = Me_3SiCl + Et\cdot} \qquad (1)$$

$$\mathrm{2Me_3Si\cdot = Me_3Si{-}SiMe_3} \qquad (2)$$

The value reported here for gas-phase recombination and the value obtained by Frangopol and Ingold[5] for a solution differ considerably from the figure of $10^{5\cdot5}$ cm^3 mol^{-1} s^{-1} calculated by Thynne from the rate of decomposition of hexamethyldisilane reported by Davidson and Stephenson.[8] We have re-estimated the entropy of hexamethyldisilane to be 501 J mol^{-1} K^{-1} using disilane as a model. The entropy of trimethylsilyl radicals can be estimated to be 336 J mol^{-1} K^{-1}. From these values, the pre-exponential factor for the decomposition of hexamethyldisilane was calculated to be $10^{18\cdot3}$ s^{-1}. This is greater than the experimental value[8] of $10^{13\cdot5}$ s^{-1} and is also larger than $10^{16\cdot3}$ s^{-1} found for hexamethylethane, the analogous carbon compound, from its decomposition in shock waves.[9]

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