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Reaction of Hydrogen Atoms with Hexamethyldisilane

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The reaction of hydrogen atoms with hexamethyldisilane has been studied by pulsed, mercury-sensitized photolysis experiments using Lyman α resonance absorption and resonance fluorescence detection of H atoms. At room temperature it proceeds exclusively according to $H + (CH_3)_3SiSi(CH_3)_3 \rightarrow (CH_3)_3SiH + (CH_3)_3Si$ (1) with a rate constant $k(1) = (3.55 \pm 0.25) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} ($T = 295$ K). The temperature dependence of the rate constant in molecular units can be expressed by $\log k(1) = (-10.9 \pm 0.1) - [(1770 \pm 50)/(2.30T)]$. The pseudo-first-order rate constant for H atom disappearance, k^1, shows a dependence on the initial hydrogen atom to substrate concentration ratio. This is explained by two competing reaction channels for the disappearance of the trimethylsilyl radical: bimolecular combination ($k(2)$) and combination of hydrogen atoms with trimethylsilyl radicals yielding trimethylsilane ($k(3)$). From the intensity dependence of k^1 and under the assumption that only reactions 1, 2, and 3 are operative, model calculations yield $k(3) = (2 \pm 1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, while for $k(2)$ only an upper limit of $\leq 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} can be given. Thermochemical calculations suggest that the true value for $k(2)$ is lower, probably close to the liquid phase values.

Introduction

The reaction of hydrogen atoms with alkanes generally proceeds by hydrogen abstraction, or using a different terminology,[1] by a substitution reaction (S_H2 reaction) at one of the hydrogen centers of the alkane

$$H + HX \rightarrow [H\text{–}H\text{–}X] \rightarrow H_2 + X$$

where $X = C(R)_3$. Substitution at a carbon center

$$H + XH \rightarrow [H\text{–}X\text{–}H] \rightarrow HX + H$$

will be observed only with translationally hot hydrogen atoms. This is due to the higher activation energy needed for the latter process.[2] One might expect that the difference in activation energies for substitution reactions at H and X centers becomes smaller if there are low-lying unoccupied orbitals available on X.[3] Substitution at an X center should become more favored with second or higher row elements; such processes have indeed recently been characterized in the case of sulfur.[4,5]

Following this line of reasoning it was postulated[6–8] that for $X = Si(R)_3$ even the abstraction reaction proceeds by an attack of hydrogen atoms at Si yielding a pentacoordinated silicon intermediate. However, experimental or theoretical support for this hypothesis could not be found.[9–12]

There have been two publications reporting that, at least in the case of disilanes, substitution reactions at a silicon center are taking place. From the reaction of iodine atoms with hexamethyldisilane in the gas phase at elevated temperatures Band and Davidson[13] obtained trimethylsilyl iodide as the only product. This was interpreted in terms of substitution of the $(CH_3)_3Si$ group by iodine atoms. The rate law as well as the Arrhenius parameters supported this interpretation. A similar observation was made by Strausz and co-workers[14] who investigated the reaction of hydrogen atoms with disilane-d_6. Besides the expected product HD, appreciable amounts of SiD_3H were found as well. S_H2 reactions at silicon have also been reported for the liquid phase.[15]

From a preceding study of the mercury-sensitized photolysis of hexamethyldisilane[16] one already knows that at low temperatures the reaction of hydrogen atoms with hexamethyldisilane proceeds exclusively by a substitution reaction yielding trimethylsilane and trimethylsilyl radicals. We decided to use this clean reaction for a kinetic characterization of the substitution reaction at a silicon center.

Experimental Section

Absolute rate constants were measured by a pulsed photolysis method. The apparatus has been described,[17] thus only the main features will be mentioned with a more detailed description of the improvements since added. Our setup is very similar to a conventional flash photolysis system employing resonance absorption and/or resonance fluorescence for the detection of atoms, the main difference being the production of H atoms by means of pulsed mercury resonance radiation, a method pioneered by Michael and co-workers.[18] There are no principal problems in pulsing a low-pressure arc, provided the dark periods are kept short in order to avoid cooling of the lamp. Due to the slow disappearance of the radicals, high repetition rates are not feasible in our kinetic experiments. Therefore, a combination of a mechanical shutter (Compur-3) and an electrical shut down of the lamp has been used. The light pulses are generated by opening the shutter with a moderately fast rise time of 2–3 ms. After a preselected time interval, typically 5 ms, the lamp is electrically shut down with a light falltime of 10 μs. Immediately after the electrical shut down the mechanical shutter closes and the mercury arc is turned on again. The pulse frequency lies in the range of 1–0.1 s^{-1}.

The gases ((1–1.2) × 10^5 Pa of He, 100–1000 Pa of H_2, 1–10 Pa of substrate) and mercury vapor are premixed in a 20-L vessel and then allowed to flow through the reaction chamber to ensure turnover of the content after each pulse. The pressure in the cuvette (0.7 bar) is kept constant by means of an automatic pressure controller (MKS 250A).

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TABLE I: Comparison of Experimental and Calculated Wall Constants k_w (s^{-1}) for Different Delay Times in a Cylindrical Cell with the Dimensions $r = 2.5$ cm, $l = 5$ cm

	delay time/s			
	0	0.125	0.25	0.5
expt	3.75 ± 0.05	4.68 ± 0.04	5.08 ± 0.06	5.33 ± 0.19
calcd	4.29	4.82	5.06	5.14

The H atoms are detected by means of a sensitive dc discharge lamp.[17] After the radiation passed through the reaction chamber and was dispersed by a 0.5-m vacuum-UV monochromator (McPherson 235), it was detected by a solar blind photomultiplier (EMR-614G). Pulse counting in combination with multichannel scaling and subsequent computer processing of the data is employed. The whole detection system is triggered by the trailing edge of the photolysis pulse.

The absorbed intensity of the mercury lamp has been determined by propane actinometry.[19] The extrapolated rate for H_2 formation for zero illumination time was assumed to proceed with a quantum yield of unity. For the unattenuated light beam an absorbed intensity of $(1.0 \pm 0.1) \times 10^{14}$ cm^{-3} s^{-1} has been obtained. Reproducible attenuation of the mercury resonance radiation was achieved by interposing wire meshes between lamp and photolysis cell; their transmission has also been measured by propane actinometry and found to be $(0.48)^n$ where n is the number of meshes.

An advantage of our setup is the fact that it uses a clean source of hydrogen atoms not accompanied by other radicals which could complicate the kinetics. Furthermore, the light pulses are obtained with high reproducibility (~5% pulse-to-pulse variation), absolute intensity calibrations are easily performed, and systematic variations of the mercury light intensity by two orders of magnitude can be done routinely.

On the other hand, this generation of H atoms causes difficulties: formation of the atoms by absorption of the mercury resonance line leads to an inhomogeneous H atom distribution along the cell axis. This causes a nonexponential decay of the hydrogen atoms due to diffusion of the H atoms into the observation volume, especially easily discernible for low first-order rate constants. If one calculates "first-order rate constants" from such curves the value obtained depends on the delay time between the end of the photolysis pulse and the beginning of the observation. For the wall constant k_w (no substrate) we observed the values given in Table I. We tried to simulate the experiments by solving the diffusion equation for cylindrical symmetry with the boundary condition of zero hydrogen atom concentration at the walls. Because there is no easy way to determine the distribution of the initial hydrogen atom concentration we assumed a simple exponential dependence on the distance along the cylinder axis and used the extinction coefficient as an adjustable parameter. The value of the diffusion coefficient used is $D = 2.25$ cm^2 s^{-1}.[20] The agreement between experimental and calculated values can be seen from Table I. The increase of k_w with increasing delay time should be independent of mercury light intensity as has indeed been observed. To obviate objections that the agreement is fortuitious, we built a different cell, again of cylindrical shape but of much shorter length (1 cm vs. 5 cm). Experimentally a value $k_w = 25.8$ s^{-1} was obtained while the calculations using the same input parameters as above gave 25.3 s^{-1}. We are therefore quite confident that our model allows us to understand and correct for most of the deficiencies in our setup. This kind of model calculations was used to estimate the errors one makes in extracting first-order rate constants from such time resolved absorption (or fluorescence) curves. The result found was that the amount of correction depends on the magnitude of the first-order rate constant: while for $k^1 = 10$ s^{-1} the correction amounts to 30%, it decreases to 6% for $k^1 = 100$ s^{-1}. In all cases the correction leads to an increase in the rate constant.

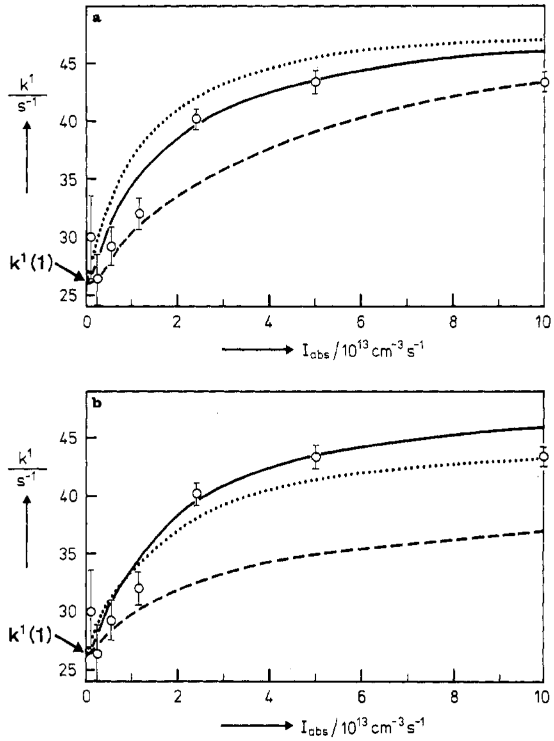

Figure 1. Dependence of the pseudo-first-order rate constant k^1 on mercury light intensity; (a) comparison with calculated values $k(1) = 3.5 \times 10^{-14}$ cm^3 s^{-1}, $k(2) = 5 \times 10^{-12}$ cm^3 s^{-1}, $k(3) = 3 \times 10^{-10}$ cm^3 s^{-1} (····), 2×10^{-10} cm^3 s^{-1} (—), 1×10^{-10} cm^3 s^{-1} (----). (b) Comparison with calculated values $k(1) = 3.5 \times 10^{-14}$ cm^3 s^{-1}, $k(3) = 2 \times 10^{-10}$ cm^3 s^{-1}, $k(2) = 5 \times 10^{-10}$ cm^3 s^{-1} (----), 5×10^{-11} cm^3 s^{-1} (····), 5×10^{-12} cm^3 s^{-1} (—).

Hexamethyldisilane was of commercial origin and contained two impurities: 0.3% hexamethyldisiloxane and 0.03% 2,2,3-trimethyldisilapentane-2,4 as determined by GC. Prior to use, He (99.96%) and H_2 (99.999%) were passed through molecular sieves which were cooled by liquid nitrogen.

All errors quoted refer to single standard deviation.

Results and Discussion

Mercury-sensitized photolysis of H_2 in the presence of small amounts of hexamethyldisilane (typically 1 mol %) yields trimethylsilane as the only product at room temperature in agreement with earlier findings.[16] The only conceivable reaction explaining this result is a displacement reaction

$$H + (CH_3)_3SiSi(CH_3)_3 \rightarrow (CH_3)_3SiH + (CH_3)_3Si \quad (1)$$

followed by the combination of the trimethylsilyl radicals forming hexamethyldisilane

$$2(CH_3)_3Si \rightarrow (CH_3)_3SiSi(CH_3)_3 \quad (2)$$

At higher temperatures other products resulting from hydrogen abstraction from the methyl groups are formed as well, but up to 500 K they are only of minor importance.

In the course of the experiments it became clear that the measured pseudo-first-order rate constant for the disappearance of H atoms, k^1, depends on the mercury light intensity (see Figure 1). Such a case is always expected to happen if both reaction 1 and the radical combination reaction 2 are so slow that the presumably fast atom radical combination reaction 3 comes into play.

$$H + (CH_3)_3Si \rightarrow (CH_3)_3SiH(v) \quad (3)$$

One derives within this mechanism for high mercury light intensities

$$k^1 = 2k(1)[(CH_3)_3SiSi(CH_3)_3] = 2k^1(1)$$

assuming that reaction 2 is negligible as compared to reaction 3

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and, in addition, making the steady-state assumption for $(CH_3)_3Si$. At low intensities reaction 3 will become unimportant and k^1 will be given by

$$k^1 = k(1)[(CH_3)_3SiSi(CH_3)_3] = k^1(1)$$

At intermediate intensities, k^1 will have values between $k^1(1)$ and $2k^1(1)$. In addition, there will be deviations from a first-order behavior. Such deviations, although small, have indeed been seen in model calculations; within our experimental accuracy they could not be detected in the actual experiments.

However, there exists a very large value for $k(2)$ in the literature[21] which contradicts the above conjecture. On the other hand, this value has been questioned by a number of authors.[17,22-24] In the liquid phase the reported values for reaction 2[25,26] are two orders of magnitude lower than the gas-phase value. Initially, it had been thought that a value for $k(2)$ could be extracted from computer modeling of the intensity dependence of k^1. The reactions which have to be considered are the displacement reaction 1, the bimolecular disappearance of the trimethylsilyl radicals, and the atom molecule combination 3. There is no agreement in the literature as to what extent reaction 2 represents the bimolecular disappearance of the trimethylsilyl radicals. Tokach and Koob[27] find a large portion of disproportionation

$$2(CH_3)_3Si \rightarrow (CH_3)_3SiH + (CH_3)_2Si{=}CH_2 \qquad (4)$$

Strausz et al.[22] give a small value for the ratio of disproportionation to recombination, while we[24] did not find any disproportionation products at all. In all our experiments we find for the ratio of the high-intensity pseudo-first-order rate constant to the extrapolated zero intensity rate constant a value of 2.0 ± 0.2 (see Figure 1), as would be expected from a mechanism involving only reactions 1–3. This figure supports a small value for the ratio of disproportionation to recombination, because from our experimental evidence on the fast addition of CH_3 radicals to the Si=C double bond it has to be surmised that this is also true for hydrogen atoms.[24] We have therefore neglected the disproportionation reaction in our calculations. Concerning reaction 3 it is known[28,29] that the vibrationally hot $(CH_3)_3SiH(v)$ molecules are stabilized even at pressures as low as 500 Pa. Besides reactions 1–3 the diffusion of the H atoms to the wall was also taken into account in our calculations. The results show quite clearly that the shape of the curve k^1 vs. intensity is sensitive to the value of $k(3)$ and much less so for $k(2)$, except for very high values of $k(2)$ (see Figure 1). In all our experiments we find for reaction 3 a value of $k(3) = (2 \pm 1) \times 10^{-10}$ cm^3 s^{-1}. For reaction 2 we can give only an upper limit of $\leq 5 \times 10^{-11}$ cm^3 s^{-1}, all smaller values fit the experimental curves equally well. A thermochemical calculation suggests that the true value is much lower than our upper limit. The rate constant $k(-2)$ has been measured by Davidson and Howard[23] in the temperature range 700–900 K. The entropic part of the equilibrium constant for reaction 2 can be calculated by means of the values given by O'Neal and Ring.[30] Two limiting values may be envisaged: free rotation of the methyl groups in the trimethylsilyl radical or hindered rotation with the same barrier height as in hexamethyldisilane (assumed to be equal to the barrier height in methylsilane, the only measured value).[31] One then finds 4.5×10^{-15} cm^3 s^{-1} $\leq k(2) \leq 1.6 \times 10^{-12}$ cm^3 s^{-1}. This value just overlaps with another estimate made in the system $(CH_3)_3Si + D_2 \rightleftarrows (CH_3)_3SiD + D$ with 1×10^{-12} cm^3 s^{-1} $\leq k(2) \leq 1 \times 10^{-11}$ cm^3 s^{-1}.[17] One may conclude that the value for $k(2)$ as determined by Cadman, Tilsley, and Trotman-Dickenson[21] is too large and that the true value probably lies close to the liquid-phase values as well as to the gas-phase values for the corresponding carbon radicals.[32,33]

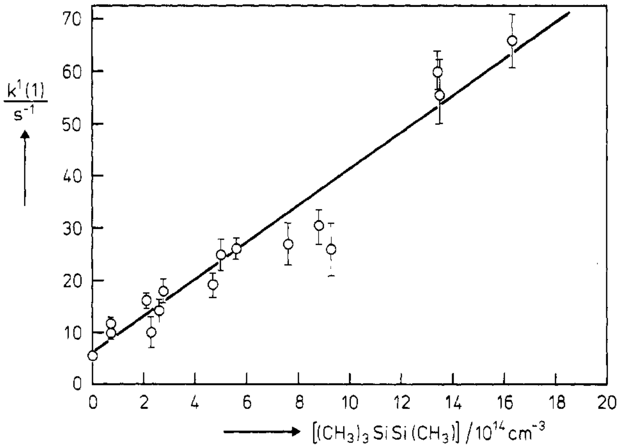

Figure 2. Dependence of the pseudo-first-order rate constant $k^1(1)$, extrapolated to zero light intensity, on hexamethyldisilane concentration. T = 295 K.

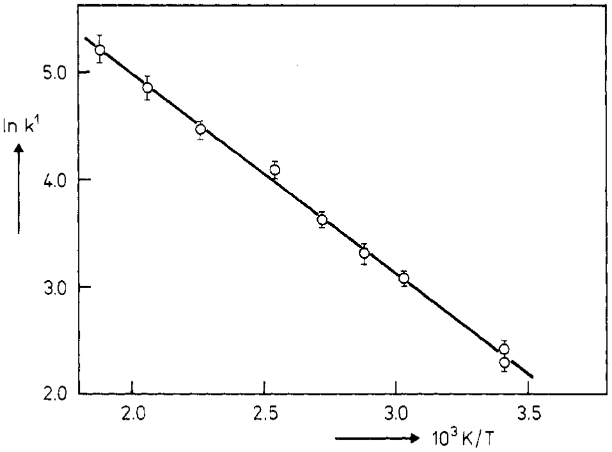

Figure 3. Arrhenius plot for k^1.

In Figure 2 the first-order rate constants for zero mercury light intensity $k^1(1)$ are plotted as a function of the hexamethyldisilane concentration. A value for $k(1) = (3.55 \pm 0.25) \times 10^{-14}$ cm^3 s^{-1} at 295 K is obtained. The temperature dependence of $k(1)$ was measured at a fixed mercury light intensity ($I_{abs} = 3.4 \times 10^{13}$ cm^{-3} s^{-1}). As already pointed out in ref 34 no difference in the activation energy was found within our error limits using either the extrapolated rate constants or those obtained at a fixed light intensity. From the Arrhenius plot in Figure 3 an activation energy $E_A(1)$ = 14.7 ± 0.4 kJ mol^{-1} is obtained. With this and the room temperature value for $k(1)$ the preexponential factor is estimated to be log $A(1)$ = 10.9 ± 0.1 cm^3 s^{-1}. Activation energy and the A factor for the displacement reaction are not too different from those for the hydrogen abstraction from monosilanes.[35] This raises

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the question as to why this type of process is observed in disilanes but not in monosilanes. A satisfactory answer to this question requires an understanding of the mechanism of the displacement reaction. This is not yet the case but one factor can be identified if the displacement reaction is formally thought of consisting of two steps: (1) interaction of the H atom with the molecule and (2) bond breaking of the silicon center and the leaving group. The bond dissociation energy of the Si leaving group bond will then be an important factor for the occurrence or nonoccurrence of the displacement reaction. One reason for observing this process only in disilane would then be the lower Si–Si bond dissociation energy as compared to the H-, CH_3-, and Cl-substituted monosilanes so far studied.[36]

Registry No. H_2, 1333-74-0; H, 12385-13-6; $(CH_3)_3SiSi(CH_3)_3$, 1450-14-2; $(CH_3)_3Si$, 16571-41-8.

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Crystal Energy Calculations for Strontium Ions in Zeolite A

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Energy-minimization calculations based on two-body electrostatic and repulsive terms predict that transfer of one Sr^{2+} from a 6-ring to an 8-ring site in dehydrated Sr-exchanged zeolite A increases the lattice energy by 4 eV. This agrees with the X-ray diffraction data at room temperature for the absence of Sr in 8-ring sites. Transfer of up to 4 Sr^{2+} from the sixteen 6-ring sites projecting into the supercage to the sixteen 6-ring sites projecting into the sodalite unit produces little change in the lattice energy (0.1 eV), but a weak energy minimum was found for transfer of 2 Sr^{2+}. Although this matches the observed distribution with four-fifths of the Sr^{2+} in the supercage and one-fifth in the sodalite unit, the effects of thermal energy and of perturbations from strict alternation of Si and Al atoms need consideration.

Introduction

Computer modeling based on minimization of total energy is useful for complex problems involving inorganic crystal structures.[1,2] Particularly important is the addition of a repulsive energy to the electrostatic energy for each pair of ions. A three-body term is not presently included. Predicted distributions[3] of K ions in dehydrated K-exchanged zeolite X matched those found experimentally. We now consider the distribution of Sr^{2+} ions in dehydrated Sr-exchanged zeolite A. The first structure determination[4] of an unanalyzed crystal placed five Sr atoms in the eight six-ring sites and the sixth Sr atom for the 12-Å pseudocell in an 8-ring site; this distribution was supported by a theoretical study.[5] A second structure determination[6] of an analyzed crystal of composition near $Sr_{5.7}Al_{11.4}Si_{12.6}O_{24}$ showed that all 5.7 Sr atoms of the pseudocell were associated only with the 6-rings, with 4.5 Sr at position (1) projecting into the supercage and 1.2 Sr at position (2) displaced into the sodalite unit. We now investigate the total energies for electrostatic and repulsive terms, first for cation distributions between 6- and 8-ring sites, and then for cation distributions involving opposite sides of the 6-rings. Following ref 5 the 8-ring site was placed at position (3) with coordinates 0.072, 0.448, 0.448 in the 12-Å pseudocell. The present calculations were made for the unique subunit of the 24-Å face-centered cell with strict Si,Al alternation (Figure 1). This unit contains 48 tetrahedral sites and 12 Sr^{2+} ions.

Techniques

All calculations were made with the METAPOCS code,[2] which is a general computer program for crystal structure prediction using energy minimization. The program calculates electrostatic energies by using the Ewald transformation technique. Short-range energies are evaluated from parameterized analytical potentials. More detailed discussions[2,7,8] give a full account of the minimization techniques and their application to crystal structure prediction. Interaction potentials between framework ions are based on the ionic model with formal changes. The $Si^{4+}\cdots O^{2-}$ and $Al^{3+}\cdots O^{2-}$ shortrange potentials were taken from ref 7 and 8. The

TABLE I: Parameters for Interatomic Potentials of the Form $V(r) = A\exp(-r/\rho) - Cr^{-6}$

interaction [a]	A, eV	ρ, Å	C, eV Å^{-6}
$Si^{4+}\cdots O^{2-}$	998.98	0.34550	0.00
$Al^{3+}\cdots O^{2-}$	1460.30	0.29912	0.00
$Sr^{2+}\cdots O^{2-}$	1952.39	0.33685	19.22
$O^{2-}\cdots O^{2-}$	22764.0	0.1490	27.88

[a] Cation···cation short-range potentials are ignored.

TABLE II: Calculated Lattice Energies for Sr-Exchanged Zeolite A, after Energy Minimization

	lattice energy, eV	
no. of Sr atoms in site (1)	zero occupancy of site (3)	after removal of one Sr to site (3)
12	−5204.58	−5200.61
11	−5204.49	−5200.84
10	−5204.61[a]	−5200.28
9	−5204.46	−5200.48
8	−5204.48	−5200.44

[a] Most stable.

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