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Scavenger Assisted Trapping of Atomic Hydrogen in Si_8O_{12}-Cages

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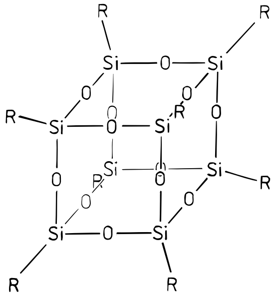
The trapping of hydrogen atoms generated by γ-irradiation of different compounds containing the cube-shaped Si_8O_{12}-cage was investigated by means of electron spin resonance (ESR). The trapped hydrogen atoms were found to originate from the organic substituents of the cages. It was shown that intermolecular processes are involved in trapping. This was done by means of a crossover experiment in which d_{72}-octakis-(trimethylsiloxy)octasilsesquioxane (i.e., d_{72}-Q_8M_8) and h_{72}-Q_8M_8 were used. Most surprising, the relative yield of trapped hydrogen atoms is considerably increased by radical scavenging additives (e.g., NO, O_2, and I_2) present during γ-irradiation. In the presence of radical scavengers, the dose dependence of $[H_{tr}^{\bullet}]$ in, for example, octapropyloctasilsesquioxane becomes almost linear, whereas in the absence of any scavengers it reaches a much lower and quasistationary level. Only for octahydridooctasilsesquioxane (HT_8) and octamethyloctasilsesquioxane (MeT_8) the yields of atomic hydrogen are not noticeably affected by radical scavengers. This is probably because the scavengers cannot enter the crystal lattices of HT_8 and MeT_8. If radical scavengers are absent, radicals generated from the substituents can be detected at room temperature for long periods of time. Elemental iodine facilitates the trapping of hydrogen atoms even in solutions of silsesquioxanes in cyclohexane. Moreover, there are radiation induced processes, which remove trapped hydrogen atoms from their traps, so the detected concentration appears to be a net effect. Deoxygenated solutions of irradiated specimen advantageously allow the observation of a well-resolved ^{29}Si-superhyperfinestructure (shfs). The comparison of the experimental shfs pattern with the theoretically expected one proves convincingly the encapsulation of hydrogen atoms in intact Si_8O_{12}-units. The values of the shf-coupling constants depend on the nature of the substituents attached to silicon and decrease with increasing temperature. The thermal decay process of $H^{\bullet}$ trapped in the solid state is not affected by the atmosphere present and follows first-order kinetics. This corresponds with the uniform trap sites. The activation energy for this process is estimated to 109.6 ± 3.1 kJ/mol ($343 \le T \le 387$ K) in the case of $H^{\bullet}$:Q_8M_8. The satellites of the hydrogen hyperfine transitions were shown to be spin-flip satellites. Proposals in order to explain the observed effects are made.

1. Introduction

Compounds containing the cube-shaped Si_8O_{12} unit[22] (see Chart 1) have continuously attracted attention since their discovery about 50 years ago. The attractiveness of polyhedral polysilsesquioxanes, polysilicates, and related compounds is due to their fascinating physical and chemical properties[1] and their appealing aesthetic geometry. In 1994, Sasamori, Okaue, Isobe, and Matsuda[2] discovered another interesting feature of one of these compounds. They found the trimethylsilylated derivative of the double-four ring (D4R) silicate (Q_8M_8) able to stabilize radiolytically generated hydrogen atoms at room temperature. Up to now there are only a few examples[3] of hydrogen atoms observable at ambient temperatures. The most prominent one is $H^{\bullet}$:CaF_2.[4]

The most surprising fact Sasamori et al. reported on was that the "jacketed hydrogens" are even stable in etheral solution.[2] These first results raised a lot of questions; some of them we dealt with in the present contribution: 1. Is it possible, to substantiate the essentially chemical reasoning of Matsuda et al.[2] concerning the entrapment in cages by spectroscopic means? 2. What is the physical origin of the satellites in the spectra of the solids already mentioned by Matsuda et al.?[2] 3. Which factors influence possibility and effectiveness of trapping? What about trapping of hydrogen atoms by the cages in solutions? 4. Which conditions have to be fulfilled by hydrogen atoms to get trapped and what can be stated about the mechanism?

CHART 1. Structures and Denominations of the Substances Used[a]



R = H −HT_8
R = D −DT_8
R = methyl −MeT_8
R = ethyl −EtT_8
R = propyl −PrT_8
R = cyclohexyl −$CyxT_8$
R = vinyl −ViT_8
R = phenyl −PhT_8
R = $OSi(CH_3)_3$ −h_{72}-Q_8M_8
R = $OSi(CD_3)_3$ −d_{72}-O_8M_8

[a] Structural details (i.e., bond angles and bond lengths) have been simplified for clarity.

2. Experimental Section

All compounds were synthesized according to previously published procedures.[5] The silsesquioxanes were obtained from

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the commercially available trichlorosilanes (R = H, Me, Et, Pr, Vi, and Ph). Cyclohexyltrichlorsilane[6] was conveniently prepared by γ-radiation induced addition of cyclohexene to $HSiCl_3$. h_{72}-Q_8M_8 was obtained by trimethylsilylation of tetramethylammonium-D4R-silicate.[7] DT_8 was made from HT_8 and D_2 (>99.8% D, Aldrich) in the presence of Pd/C (5%, Aldrich) and characterized by IR: ν(Si-D) 1665 cm^{-1} (vs).[8]

d_{72}-Q_8M_8 was obtained starting from CD_3MgI (Aldrich) by the following reactions, which are known from the literature[9] for the corresponding protium compounds:

$$CD_3MgI \xrightarrow{PhSiCl_3} (CD_3)_3\mathbf{Si}C_6H_5 \xrightarrow{CF_3SO_3H} (CD_3)_3\mathbf{Si}\ O_3SCF_3 \xrightarrow{NEt_3HCl}$$

$$(CD_3)_3\mathbf{Si}Cl \xrightarrow{NMe_3 \rightarrow O} (CD_3)_3\mathbf{Si}Cl{\cdot}(CH_3)_3N \rightarrow O \xrightarrow{1/8\ H_8Si_8O_{12}} [(CD_3)_3\mathbf{Si}O]_8Si_8O_{12}$$

This way was chosen in order to get a higher isotopic yield compared with the procedure given in ref 7a.

The silsesquioxanes as well as iodine were sublimed twice in vacuo prior to use. Cyclohexane was of analytical grade and used without further purification; h_{72}-Q_8M_8 and d_{72}-Q_8M_8 were recrystallized from acetone.

Solid samples were γ-irradiated in sealed glass ampules (volume ca. 4−5 mL), each containing ~100 mg. Definite atmospheres were adjusted by evacuating and filling the ampules repeatedly. Rare gases (He, Ar; Messer-Griesheim) were of ≥99.999% purity; oxygen was of technical grade. Nitric oxide 5% in N_2 was purchased from Air Liquide; pure NO was obtained from this mixture by means of a cryogenic trap. Before sealing the ampules, pressure was adjusted and controlled by a capacitance manometer (Brand DVM 1). Solutions were deoxygenated by purging them for about 20 min with Ar or He (99.999%).

γ-Irradiations were carried out in a cave-type-^{60}Co source. Applied doses were determined from irradiation times and calibrated dose rates taking into account the decay of ^{60}Co. They are correct within ±5%.

ESR-spectra were recorded on a cw-X-band-spectrometer ERS-300 (ZWG, Berlin-Adlershof) equipped with a variable temperature controller. Sealed and irradiated ampules were measured after thermal elimination of paramagnetic centers generated in the glass.[23] All given relative concentrations of atomic hydrogen are mass-normalized and were determined after having exposed the spread out solid samples to air for at least 2 h. This was done in order to eliminate the influence of different amounts of adsorbed oxygen[24] on the signal intensities. Solutions of irradiated specimen were prepared from spectroscopic grade tetrachloromethane and tetrachloroethene, respectively. Oxygen was removed by purging the solutions with Ar (≥99.999%). To reduce passage effects, the modulation frequency had to be set to 20 kHz. Simulations and mathematical treatments of spectra were accomplished using *GENPLOT* (CGS Ltd., Ithaca, NY) and *Isotrop* (Dr. D. Pfeifer, BAM Berlin, Germany).

3. Results

General Remarks. Influence of Radical Scavengers and Temperature. The ability to stabilize atomic hydrogen formed upon γ-irradiation is not restricted to the trimethylsilylated D4R-silicate Q_8M_8. Also silsesquioxanes (RT_8) do so. In addition, preliminary results indicate that even a heterosilsesquioxane possessing a Si_7PO_{12}-cage[10] is able to trap atomic hydrogen.[25]

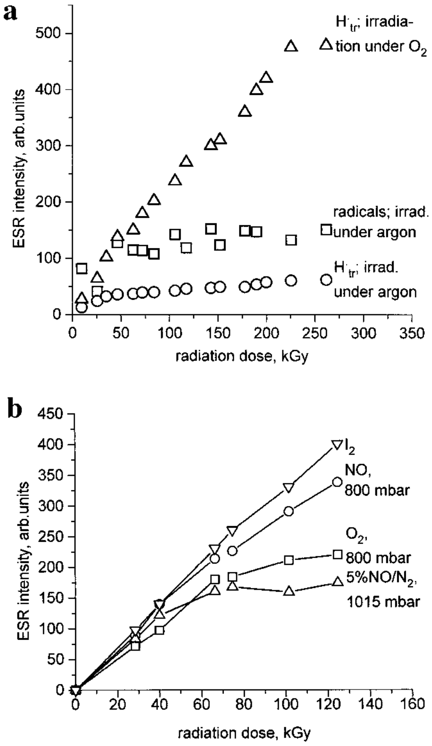

Figure 1. (a) Relative concentrations of trapped hydrogen atoms in PrT_8 samples irradiated in an oxygen (△) and argon (○) atmosphere, respectively. The relative concentration of radical species ($g' \approx 2$) formed under argon is also given (□). (b) Relative concentrations of hydrogen atoms trapped in PrT_8 as functions of the absorbed dose and the radical scavengers present.

When checking the results of Matsuda et al.,[2] an effect contrary to all common expectations was found: The relative yield of trapped atomic hydrogen was considerably higher if oxygen was present during γ-irradiation. Therefore, more detailed experiments dealing with the influence of radical scavengers were performed. As a model compound PrT_8 was used. Figures 1a,b present the corresponding results as $[H_{tr}^\bullet]$ vs γ-dose plots.

In the absence of radical scavengers the concentration of $H_{tr}^\bullet$ slowly rises with respect to the absorbed γ-dose and tends to reach a comparatively low quasistationary level.

In contrast to that, the addition of scavengers results in a rapid and almost linear growth of the concentration of $H_{tr}^\bullet$. Up to doses of 260 kGy, no quasistationary levels of $H_{tr}^\bullet$ are observed. In Figure 1a the curve denoted by squares shows the dose dependence of the relative concentration of carbon-centered radicals for samples irradiated in argon. It is worth noting that the latter concentration tends to reach a quasistationary level, too.

Figure 1b shows that NO is slightly more effective than oxygen at the same partial pressure in supporting the entrapment of hydrogen atoms. Moreover the curve for 5% NO in N_2 shows the importance of the concentration and the total amount of scavengers available in the sealed ampules.

Under the experimental conditions of the present study iodine appeared to be the most powerful supporter of the trapping. All irradiations involving iodine were performed in the presence of excess solid iodine so that the partial pressure of I_2 (i.e., 0.41 mbar at room temperature[11]) should have been constant during irradiations.[26]

Another experiment was set up to determine the response of differently substituted compounds to iodine present during irradiation and to the influence of irradiation temperature, see Figure 2. With the exception of HT_8 and MeT_8 the yield of $H_{tr}^\bullet$ is increased by I_2 and O_2 respectively; with the exception

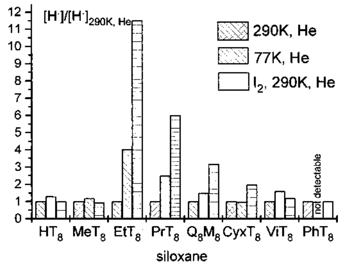

Figure 2. Influence of iodine and of the irradiation temperature on the amount of trapped hydrogen atoms in different compounds. Concentrations are normalized with respect to the amount of hydrogen atoms trapped under He at 290 K; dose: 72 kGy.

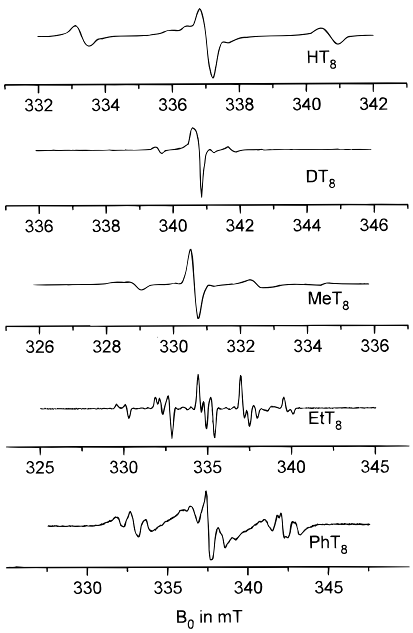

Figure 3. ESR signals of radicals ($g' \approx 2$) formed in different siloxanes upon irradiation at room temperature under exclusion of oxygen, dose: ~2 kGy.

of PhT$_8$ the trapping of $\mathrm{H_{tr}^{\bullet}}$ becomes more effective at lower temperatures.

If irradiation is performed with no scavengers added (e.g., in He, Ar, vacuum), all samples show signals of free radicals in the $g \approx 2$-region. A few of them are depicted in Figure 3. With the exception of HT$_8$, DT$_8$, and MeT$_8$ these signals vanish within a few days. If the samples are exposed to air, the signals disappear immediately. Simulation and assignment of these spectra turned out well for the cases of HT$_8$ ($\mathrm{O_{3/2}Si^{\bullet}}$; $\mathrm{O_{2/2}Si^{\bullet}H}$, $a_H = 7.4$ mT), DT$_8$ ($\mathrm{O_{3/2}Si^{\bullet}}$; $\mathrm{O_{2/2}Si^{\bullet}D}$, $a_D = 1.16$ mT), MeT$_8$ ($\mathrm{O_{3/2}Si^{\bullet}CH_2}$, $a^{\perp}(2H) = 1.69$ mT, $a^{\|}(2H) = 2.31$ mT), EtT$_8$ ($\mathrm{O_{3/2}{-}Si{-}C^{\bullet}H{-}CH_3}$, axial symmetric; additionally something like $\mathrm{^{\bullet}CH_2CH_3}$, isotropic) and PhT$_8$ (3-silylcyclohexa-1,4-dienylradicals, $a_{iso}(2H,CH_2) \approx 4.8$ mT, $a_{iso}(2H,CH_{ortho}) \approx 0.9$ mT, $a_{iso}(2H,CH_{meta}) \approx 0.25$ mT, slightly anisotropic).[27]

Source of Trapped Hydrogen. The synthesis of perdeuterated Q$_8$M$_8$ (d_{72}-Q$_8$M$_8$) was carried out in order to determine the source of trapped hydrogen atoms and to find out more about the mechanism of trapping (crossover experiments, see below).

Figure 4a represents the overall spectrum of solid (h_{72}-)Q$_8$M$_8$; in Figure 4b the corresponding spectrum of d_{72}-Q$_8$M$_8$ is shown. Both samples were γ-irradiated under access of air. While Figure 4a displays the characteristic hyperfine doublet of hydrogen atoms ($I = 1/2$), Figure 4b represents the typical line-triplet caused by atomic deuterium ($I = 1$). This last result confirms the organic substituents to be the source of trapped hydrogen.

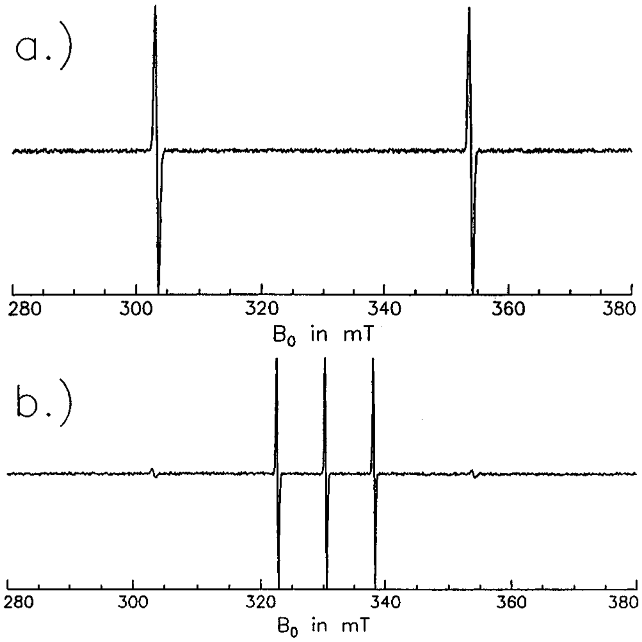

Figure 4. Spectra of irradiated solid h_{72}-Q$_8$M$_8$ (a) and d_{72}-Q$_8$M$_8$ (b). The small signals due to atomic hydrogen in (b) are likely to arise due to residual solvents, dose: ~100 kGy, room temperature.

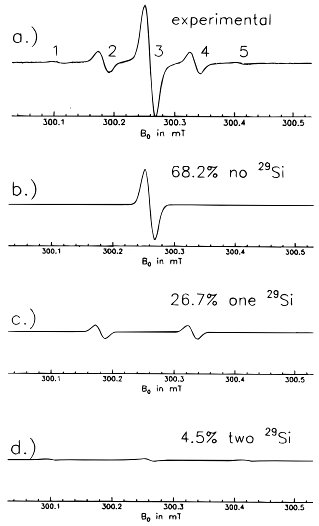

Figure 5. Super-hyperfine structure (low-field transition) due to the surrounding ^{29}Si-nuclei in EtT$_8$. (a) experimental, dose: ~100 kGy, room temperature). Traces (b−d) simulated spectra of the involved isotopomers shown true to scale.

Trapping of H$^•$ in Intact Si$_8$O$_{12}$-Units. Influences of R and T on the Superhyperfine Coupling Constant a_{29Si}. The fairly high γ-doses which had to be applied in the experiments presented in this paper led to the question of radiation induced structural alterations in the Si$_8$O$_{12}$-units themselves. Routine ^{13}C-, ^{29}Si NMR-, and FT-IR spectra did not indicate any noteworthy changes of the irradiated cages. Therefore, we tried to investigate the nature of the trapsites in more detail by means of ESR-spectroscopy of solutions. It turned out that even in oxygen-containing solutions line widths are considerably lower than those in the corresponding solids. Oxygenfree solutions of irradiated specimen (HT$_8$ and PhT$_8$ were excluded because of their poor solubility) in different solvents (e.g., CCl$_4$, C$_2$Cl$_4$) yield spectra with a pattern shown in Figure 5a. Each hydrogen hyperfine transition is further split by superhyperfine (shf) interactions with ^{29}Si-nuclei. The line widths of the individual shfs components ranged from 0.0035 mT ($\mathrm{H^{\bullet}}$:d_{72}-Q$_8$M$_8$) to 0.0095 mT ($\mathrm{H^{\bullet}}$:PrT$_8$). Table 1. contains experimentally determined[28] relative intensities of transitions marked by

TABLE 1: Experimental and Calculated Relative Intensities of the Individual ^{29}Si-Superhyperfine Transitions in Figure 5

number of peak	experimental intensity	calculated intensity
1	1.23%	1.145%
2	13.6%	13.53%
3	70.7%	70.49%
4	13.2%	13.53%
5	1.25%	1.145%

TABLE 2: Isotropic ^{29}Si-Superhyperfine Coupling Constants $a_{^{29}Si}$ for the Differently Substituted Compounds and Estimated Group Electronegativities χ_{Group} of the Corresponding Substituents

R	$a_{^{29}Si}$ (mT)	χ_{Group}
Me	0.1631	2.27
Et	0.1510	2.35
Pr	0.1570	2.35
Cyx	0.1470	2.41
Vi	0.1447	2.75
$OSi(CH_3)_3$	0.0600	4.93

TABLE 3: Approximate Line Widths ΔB_{pp} of the ESR Signals of Hydrogen Atoms Trapped in Differently Substituted Compounds in the Solid State

R	ΔB_{pp} (mT)
H	0.17
Me	0.15
Et	0.14
Pr	0.14
$OSi(CH_3)_3$	0.10
$OSi(CD_3)_3$	0.04

numbers in Figure 5a. The corresponding calculated values are in the rightmost column (see discussion).

The actual values of a_{29Si} for differently substituted compounds depend both on the chemical nature of the substituent attached to silicon and on the temperature at which they were measured. Table 2 collects experimental values of a_{29Si}. In the rightmost column approximate values of the group electronegativities of the substituents are listed.[12]

As mentioned above, the temperature also has influence on the shf-couplings. For PrT_8 dissolved in C_2Cl_4 the shf-coupling constant a_{29Si} decreased continuously from 0.159 mT (253 K) to 0.147 mT (363 K).

Satellites of H$^\bullet$-Signals and Line Widths in the Solid State. After being exposed to air, the ESR spectra of the γ-irradiated powders ($R \neq$ H, D, and Me) consisted of only two signals as expected for atomic hydrogen.The observed line widths depend on the substituents as indicated by the representative values given in Table 3. In contrast to the signal intensities, line widths in the solid state are only slightly influenced by oxygen. The line widths are mainly governed by dipolar interactions with the surrounding protons. The satellites of each of the two hyperfine signals already mentioned by Matsuda et al.[2] are confirmed to appear. Being comparatively weak in Q_8M_8, the satellites cannot be overlooked in the case of MeT_8 measured under identical conditions (access of air, low microwave power levels). The following results confirm that the satellites are spin-flip satellites: 1. The distance between the satellite lines of the hyperfine transitions was proportional to the magnetic induction at which they appear: $\Delta B_{sf} = 0.9245$ mT at 311.9 mT (low-field transition), $\Delta B_{sf} = 1.0783$ mT at 362.4 mT (high-field transition). These values are mean values of numerous measurements.

2. The ratio "intensity of the satellites/intensity of the main signal" increased with rising microwave power level. In contrast to the main signals, which reversibly gain in intensity when the atmosphere is changed from argon to oxygen (this does *not* apply to HT_8, DT_8, and MeT_8), the intensity of the satellite signals does not depend on the partial pressure of oxygen during the measurement.

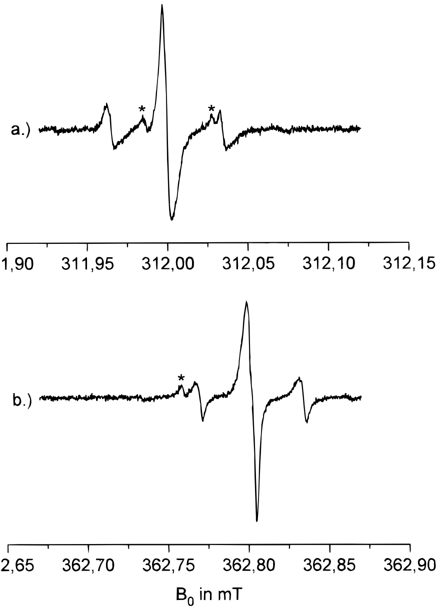

Figure 6. The low- (a) and high-field transitions (b) of hydrogen atoms generated in equimolar mixtures of h_{72}-Q_8M_8 (a) and d_{72}-Q_8M_8, dose: ~100 kGy, room temperature. The asymmetry arises from the superposition of spectra of H atoms trapped in either h_{72}-Q_8M_8 (a) or d_{72}-Q_8M_8. The asterisks indicate signals due to H$^\bullet$:$[(CD_3)_3SiO]_7\mathbf{H}[Si_8O_{12}]$.[21] The doublets arise from the superhyperfinesplitting caused by hydrogen directly attached to silicon (marked by bold H in the formula; $a_H \approx 0.0353$ mT).

3. In all cases the satellites of the high-field signal are less intense than those of the low-field signal. Relative intensities of the satellites depend on the chemical nature of substituents attached to silicon because of different mean distances between neighboring protons and the trapped atomic hydrogen.

4. Switching to the perdeuterated d_{72}-Q_8M_8, no satellites could be detected about 0.5 mT apart from each of the hyperfine signals. The corresponding deuterium flip signals are partly obscured by the line width of the main signals.

Proof for the Involvement of Intermolecular Processes in Trapping. To find out whether intermolecular processes are involved in the trapping processes, crossover experiments using mixtures of equivalent amounts d_{72}-Q_8M_8 and h_{72}-Q_8M_8 were performed. An equimolar mixture was cocrystallized from pentane in order to ensure intimate mixing and subjected to γ-irradiation under access of air.

The signals arising from trapped hydrogen atoms of an irradiated sample prepared in that way which was dissolved in deoxygenated tetrachloromethane are shown in Figure 6. Both the high- and the low-field transition appear to be asymmetric with respect to line form. This is caused by the superposition of the spectral patterns of H$^\bullet$: h_{72}-Q_8M_8 and H$^\bullet$: d_{72}-Q_8M_8. The narrower lines of H$^\bullet$: d_{72}-Q_8M_8, compared to H$^\bullet$: h_{72}-Q_8M_8 and small *a*- and *g*-shifts due to secondary isotope-effects, are considered to be the main reasons for this effect. This result is substantiated by the analysis of the corresponding signals of atomic deuterium (data not shown).

Thermally Induced Decay of the Trapped Hydrogen Atoms. The thermal stability of trapped hydrogen atoms in the γ-irradiated solid compounds was determined by means of in situ ESR-experiments at elevated temperatures (343−387 K). Interestingly, the decay process in the solid state is not noticeably affected by the atmosphere (Ar and O_2 tested). The time dependency of the signal amplitudes is well described by first-order kinetics, see Figure 7. For the activation energy of this process in the case of H$^\bullet$:h_{72}-Q_8M_8 a value of 109.6 ± 3.1

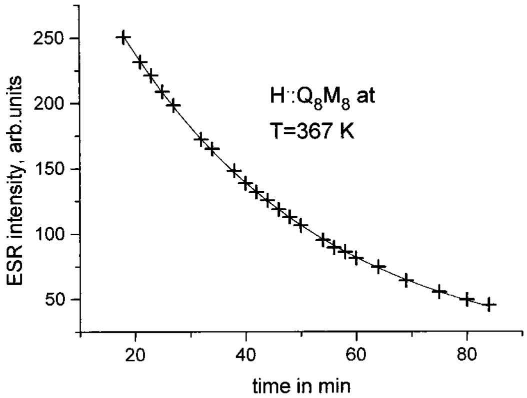

Figure 7. The thermal decay of hydrogen atoms trapped in Si_8O_{12} cages (x) is well described by first-order kinetics. The underlying curve was fitted assuming $y = ae^{-kt}$.

kJ/mol in the temperature range from 343 to 387 K was estimated from an Arrhenius plot.

γ-Irradiation of Solutions. Surprising results were obtained when subjecting cyclohexane solutions containing either EtT_8 or PrT_8, which was previously irradiated as a solid and therefore already contained trapped hydrogen atoms, to γ-irradiation. Table 4 summarizes the experimental conditions and the outcomes. H:PrT_8 stands for the preirradiated PrT_8 possessing an intensive $H_{tr}^\bullet$-signal. The dose absorbed by the sample was 120 kGy.

Only in the presence of the radical scavenger I_2 there is a net trapping of atomic hydrogen.[29] The involvement of radiation induced processes, which remove formerly trapped hydrogens from the cages is clearly shown by experiments 4 and 5.

4. Discussion

Spectral features encountered in the irradiated solids will be discussed first. The symmetric satellites of each of the hydrogen hyperfine signals were already mentioned by Matsuda et al.[2] However, they did not definitely assign them to either ^{29}Si-superhyperfine structure or to spin-flip satellites. On the basis of the experimental facts presented here, the satellites are proven to be spin flips by nature. A more detailed examination of the presented systems seems promising, because of the known geometry[13] of the trap sites and their surprising thermal and chemical stability which makes them easier to handle than most of the formerly investigated systems[14] showing spin flips.

Additional evidence for the satellites being spin-flips is that such signals could not be detected in fluid solutions. This is in accordance with the underlying dipolar interactions[15] being averaged out by rapid tumbling of the cage molecules in solution. In any case the lines of the ESR spectra obtained from solutions of irradiated compounds are narrower than in the corresponding solids. Removing the dissolved oxygen from the solutions results in further narrowing of the lines and allows the resolution of the isotropic ^{29}Si-shfs. The resulting five-line pattern can be explained quantitatively by taking into account both the relative abundance of ^{29}Si-containing Si_8O_{12} isotopomers (^{29}Si: 4.67%) and their expected spectral patterns, see Figures 5b−d). The good accordance of the experimental with calculated values (see Table 1) justifies the conclusion, that the hydrogen atoms are entrapped exclusively in structurally intact Si_8O_{12}-units. Similar arguments concerning other polyisotopic systems allowed Foner et al. and Morton et al. to figure out the trap sites of hydrogen atoms in solid rare gases (e.g., $H^\bullet$:Kr and $H^\bullet$:Xe).[16,17] Systems as for instance $H^\bullet$:CaF_2[4] and U-centers in alkali halides are classical examples for the analysis of the surroundings of paramagnetic centers. The most recent example is given by Miyazaki and Shevtsov[18] concerning the trapsites of photochemically generated hydrogen atoms in solid $^{14}N_2$ at 4.2 K.

The isotropic shfs observed in solutions is presumably caused by the Pauli repulsion forces. Adrian[19] thoroughly dealt with their influence on the shfs in “nonclassically bonded” systems. The cause for the variation of the shfs coupling constant with the substituents attached to the cages has to be attributed rather to electronic than to geometrical[13] effects. This point of view becomes reasonable, if one brings the observed shfs constants a_{29Si} in relation to the estimated group electronegativities χ_{Group} of the substituents: the higher χ_{Group}, the more a_{29Si} decreases.

From an ESR-spectroscopic point of view one can expect small spectral differences between $H^\bullet$ trapped in cages bearing deuterated and protonated substituents, respectively. The most suitable candidates for crossover experiments were therefore h_{72}-Q_8M_8 and d_{72}-Q_8M_8 because of their extremely narrow ESR lines in deoxygenated solutions. As shown in section 3 (Results), the trapping process turned out to be essentially an intermolecular one:[30] hydrogen and deuterium atoms have not necessarily to be trapped in those very cages, from whose substituents they were “knocked off” by radiationchemical processes. This in turn implies that hydrogen atoms can cover certain distances in the solids.

In this context the findings of the experiments concerning the effects of radical scavengers present during γ-irradiation become even more surprising: Different substances, which are known to be reactive radical scavengers, were found not only to enlarge the yield of trapped hydrogen atoms (except in HT_8, DT_8, and MeT_8) but they also completely alter the dose dependence of the concentration of trapped hydrogen atoms. If the irradiation is performed without addition of scavengers (e.g., in He, Ar, or vacuum), relatively small doses result in quasistationary and comparatively low levels of [$H_{tr}^\bullet$]. In contrast, radical scavengers change the dose dependency to an approximately linear function. If the scavenger is present in excess (e.g., I_2), no quasistationary level of [$H_{tr}^\bullet$] was reached even when doses up to 250 kGy were applied.

It is worth noting that those compounds, in which the yield of radiolytically formed and trapped hydrogen atoms is not affected by the presence of scavengers during radiolysis (i.e., HT_8, DT_8, MeT_8), do not lose their free radicals (e.g., $O_{3/2}SiC^\bullet H_2$ in the case of MeT_8) upon exposure to air. Moreover, the $H_{tr}^\bullet$ in these compounds does not magnetically respond to gaseous oxygen by Heisenberg exchange noticeably. Therefore, it was concluded that molecules as, for instance, O_2, NO, and I_2 cannot enter these solids.

In the presence of elemental iodine net trapping of hydrogen atoms becomes even feasible in fluid cyclohexane solution, which was otherwise impossible. This was evidenced for the first time in the present study. Experiments concerning the radiation chemistry of cyclohexane solutions containing cages enclosing $H^\bullet$ (Table 4, experiment 5) indicate that radiation induced processes occur which cause an emptying of the formerly “filled” cages. The suspectedly low fraction of filled cages makes these processes likely to be indirect ones (i.e., processes induced by solvent-derived reactive species). Experiments concerning the stability of filled cages in solution against photochemically generated radicals (e.g., $Br^\bullet$ from Br_2; *t*-Bu−$O^\bullet$ or $HO^\bullet$ from (*t*-Bu−O)$_2$) indicate that small reactive radicals are able to empty the cages. Therefore, it seems reasonable to suppose that especially hot hydrogen atoms may figure prominently in the γ-induced processes which are responsible for emptying “filled” cages.

The findings of the experiments concerning the thermal decay of trapped hydrogen atoms differ from those published for a

TABLE 4: Experimental Conditions, Applied for the Irradiation of Cyclohexane Solutions[a]

no.	experimental conditions	signals due to $H_{tr}^{\bullet}$
1	300 mg of EtT_8, 3 mL of c−C_6H_{12}, air	not detectable
2	300 mg of EtT_8, 3 mL of c−C_6H_{12}, He-purged	not detectable
3	300 mg of EtT_8, 3 mL of c−C_6H_{12}, He-purged, 25 mg of I_2	intense signal
4	170 mg of $H{:}PrT_8$, 2 mL of c−C_6H_{12}, air	no longer detectable
5	170 mg of $H{:}PrT_8$, 2 mL of c−C_6H_{12}, He-purged	no longer detectable
6	170 mg of $H{:}PrT_8$, 2 mL of c−C_6H_{12}, He-purged, 25 mg of I_2	intense signal

[a] γ-dose: 120 kGy, Room Temperature.

variety of other systems: Whereas hydrogen atoms trapped in glassy or amorphous matrices show a more complex time−temperature behavior,[20] the uniform traps in the present case give rise to simple first-order kinetics. At this time nothing can be said about the fate of the hydrogen atoms thermally removed from the cages.

The value of the activation energy determined for this process and some more general aspects make the following hypothesis reasonable: In order to be suitable for getting trapped, the kinetic energy of hydrogen atoms has to fit an "energetic window". This means, at one hand, that they have to possess enough energy to overcome the energetic barrier to enter the cage and on the other hand their energy should not considerably exceed the activation energy mentioned above.

From the preceding facts the following conclusions may be drawn: 1. There are both positive and negative contributions to the finally detected concentration of trapped hydrogen atoms (i.e., it is a *net* effect). 2. Both the presence of radical scavengers and a lower irradiation temperature favor processes, which are responsible for filling the cages.

The way radical scavengers favor the filling is not yet fully understood. Possibly, the following points might be of importance:

1. Selective scavenging of radicals which are capable of recombining with hydrogen atoms; the selectivity could be brought about by energy dependent reaction cross-sections. 2. selective scavenging of reactive (hot) particles capable of emptying "filled" cages.

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(22) To avoid the voluminous IUPAC names (e.g., 1,3,5,7,9,11,13,15-octapropylpentacyclo-$[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]$octasiloxane) of these compounds the following designations were used, derived partly from those used in silicone chemistry: H, Me, Et, Pr, Cyx, Vi, and Ph stand for hydrogen, methyl, ethyl, propyl, cyclohexyl, ethenyl, and phenyl, respectively. T_8 stands for the cube-shaped Si_8O_{12} unit. Q_8 denotes $[Si_8O_{12}]O_{8/2}$, and M means $(CH_3)_3SiO_{1/2}$. So the example mentioned above simply writes as PrT_8.

(23) This was accomplished by thoroughly heating the upper half of the sealed ampule/ESR sample tube by means of a microburner while keeping the lower half of the tube and thereby the sample itself immersed in liquid nitrogen. After that, the tube was totally immersed in the liquid nitrogen, turned upside down and subsequently transferred to the spectrometer. The radicals in the sample itself are not affected by this procedure.

(24) Preliminary experiments using $H^{\bullet}{:}Q_8M_8$ as well as $H^{\bullet}{:}PrT_8$ have shown the adsorption equilibrium with oxygen to be reached within a few seconds. The (completely reversible) response to oxygen depends on the substituents attached to the silicon atoms of the Si_8O_{12}-cage. While the signals due to $H^{\bullet}_{tr}$ in MeT_8 and HT_8 do not respond to changes in atmosphere ($Ar \rightarrow O_2$), they do increase considerably in all other compounds covered so far. For the case of $H^{\bullet}{:}Q_8M_8$ see ref 2.

(25) The successful encapsulation in this case is indicated by the additional splitting of the H-hyperfine lines in the irradiated solid due to superhyperfine interaction with ^{31}P: $a_{31P} \approx 2.33$ mT.

(26) All substances changed color upon addition of solid iodine. Therefore, due to adsorption, the actual concentration of I_2 in/at the solid is likely to be much higher than the concentration of the gaseous scavengers. While the RT_8-type compounds turned more or less pink/red, Q_8M_8 turned yellowish brown. There is indication for iodine penetrating the bulk of the substance in case $R \neq$ H, D, Me.

(27) $O_{n/2}$ indicates *n* adjacent bridging oxygen atoms.

(28) Accomplished by nonlinear-least-squares fitting of mixed Gauss−Lorentz profiles and integration of the latter using the program package *isotrop*.

(29) Latest results obtained by γ-irradiation of $EtT_8/C_6D_{12}/I_2$ provide convincing proof for the incorporation of solvent derived as well as substituent-derived hydrogen (deuterium) atoms.

(30) This statement does not exclude the involvement of *intra*molecular processes, although they are unlikely.