Electron Spin Resonance Studies on Irradiated Heterogeneous Systems

VI. The Structure and Reactivity of Paramagnetic Centers in Silica Gel

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The paramagnetic centers formed in silica gel γ-irradiated at 77°K have been identified from ESR spectra, microwave saturation behaviour, optical and thermal bleaching properties and influence of various gel pretreatments. Four main centers are formed, namely electrons trapped at oxygen vacancy sites at $g = 2.0008$, electrons trapped at a limited number of sites, whose nature is not at present quite clear, at $g = 2.0030$, hole centers trapped on the surface of the silica gel and located near to non-bridging oxygen atoms at $g = 2.0070$, and finally centers attributed to holes located close to $^{27}$Al nuclei at $g = 2.011$.

Carbon dioxide present during the irradiation forms $CO_2^-$ radicals by trapping electrons liberated in the silica gel, while the $g = 2.0070$ centers are unaffected. This shows that in addition to a positive charge transfer to form cations and a hydrogen atom transfer demonstrated in previous papers of this series an electron transfer reaction also occurs. The reaction with other electron scavengers like oxygen and nitrous oxide was found to be more complex.

Silica gel has since long been known as a non-metal catalyst of the insulator type, whose most important characteristic is its dehydration ability. The freshly prepared gel has a cristobalite structure, consisting of $SiO_4$-tetrahedra sharing corners with the Si-O-Si bonds distorted to $180^\circ$. In the amorphous material the tetrahedra are randomly arranged into a non-periodic structure, which prevents the existence of an electronic band structure except in local crystalline regions. No discrete $Si^{4+}$ and $O^{2-}$ ions are present, but the Si-O bond is predominantly ionic in character. Defects can occur in the structure as


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distortions of the tetrahedral structural units. In gels having a high specific surface area the hydroxyl groups present on the surface and in micropores affect the properties of the gel.

In silica gels exposed to high energy radiation, electron spin resonance spectroscopy (ESR) has proved valuable in the study of the induced properties. Thus it has been reported that hydrogen adsorption and H/D exchange occur at paramagnetic hole centers localized close to aluminium impurity ions. It has been suggested that the adsorption of oxygen takes place at defects possessing an odd electron. Carbon dioxide and sulfur dioxide react with non-paramagnetic defects to produce paramagnetic species. Electron transfer occurs during UV irradiation. In one study where ethylene was adsorbed at \(-150^\circ\text{C}\) on preirradiated silica gel a reaction occurred with the hydrogen atoms present on the surface and hydrocarbon radicals were formed. Other types of study in which a two component system was irradiated have provided evidence for energy transfer to the adsorbed phase, thus affecting the yields of final products. A mechanism for the interactions involving energy transfer through mobile electrons and holes has been proposed.

In previous works several different systems have been investigated by the ESR method following irradiation at 77\(^\circ\text{K}\). The aim of the present study was to characterize as far as possible the paramagnetic defects in silica gel, both in the pure system and in the presence of low molecular weight gases known as electron scavengers.

**EXPERIMENTAL**

Silica gel of 100 - 200 mesh purchased from Kebo Co. AB, Stockholm, had a BET area of 667 m\(^2\)/g and contained as main impurities Al (350 ppm) and Fe (136 ppm). This sample was used in the experiments unless otherwise stated. In order to remove surface impurities a sample was boiled for three months in 12 N hydrochloric acid. The impurity content was not measured. Gel which had previously been heated with 15 N nitric acid for three days was refluxed twice with D\(_2\)O for 12 h. By this treatment the hydrogen atoms of the surface silanol groups are replaced by deuterium. Silica gel was also prepared from SiCl\(_4\). In this case the main impurities were Al (5 ppm) and Fe (50 ppm). The specific surface area was not determined. The silica-alumina sample contained 13 % Al. The CO\(_2\) and the N\(_2\)O gases were purified from oxygen and other substances volatile at 77\(^\circ\text{K}\) by pumping at this temperature. The gels were degassed normally at 500\(^\circ\text{C}\) for 17 - 24 h at an ultimate pressure of 10\(^{-4}\) - 10\(^{-5}\) torr. Small amounts, 0.5 - 10 %, of the gases were adsorbed on the gel in vacuum either before or after irradiation, which was carried out with a \(\gamma\)-source at a dose rate of 300 krad/h.

Irradiation and ESR measurements were usually carried out in the dark. The filtered light from a 1000 W iodine lamp was used to bleach at wavelengths \(\lambda>515\) nm and \(\lambda>1000\) nm, respectively. ESR spectra were recorded at X-band using a Varian V-4502-11 spectrometer employing 100 kHz field modulation and supplied with a V-4532 dual cavity. The number of unpaired spins in a sample was estimated as described earlier. The microwave power level was measured with a General Microwave 454 A power meter connected to the cavity arm of the bridge via a 9.3 dB directional coupler. Average g-factors were estimated by comparison with the signal of solid DPPH (\(\pi,\pi\)-diphenyl-2-picrylhydrazyl), \(g=2.0037\), at the point of intersection of the derivative spectrum with the base line. The components of the g-tensors were obtained by comparison with compiled spectra and by simulations using a computer code called MARLEF.* The line widths were measured between the maximum and minimum points of the derivative line.

* Kindly put at our disposal by Dr. Jean Maruani, Centre de M\'ecanique Ondulatoire Appliqu\'ee, Paris.
RESULTS

Spectra at 77°K. In the spectrum from silica gel irradiated at 77°K to a dose of 0.8 Mrad three lines could be resolved, centered at $g_1 = 2.0070 \pm 0.0005$, $g_2 = 2.0030 \pm 0.0002$, and $g_3 = 2.0008 \pm 0.0002$ (Fig. 1a) while at 0.1 Mrad only the two former peaks could be detected. At 10 Mrad the line at $g = 2.0030$ was almost smeared out. The line shape of the $g = 2.0070$ signal could be reasonably fitted to an axially symmetric g-tensor with the values $g_1 = 2.0062 \pm 0.0005$, $g_\| = 2.0105 \pm 0.0005$. This absorption is bleached by light with $\lambda > 1000$ nm, and is absent after illumination at $\lambda > 515$ nm. The species at $g = 2.0030$ is also bleached at the shorter wavelengths, while the absorption at $g = 2.0008$ is not much affected. After bleaching a broad background spectrum is observed at $g = 2.011 \pm 0.001$, possessing several incompletely resolved peaks separated by 8 G (Fig. 1b).

The $g = 2.0070$ and the $g = 2.0030$ signals are formed predominantly following irradiation of samples degassed at temperatures of 500°C or higher, while the $g = 2.0008$ absorption strength decreases slightly with temperature. Silica gel treated with boiling hydrochloric acid before irradiation exhibits a spectrum

![Fig. 1. a) ESR-spectrum of silica gel at 77°K and a microwave power level of about 1 mW after irradiation to a dose of 0.8 Mrad in the dark. The dashed line represents a computed lineshape with the parameters $g_1 = 2.0062$, $g_\| = 2.0105$ and a Gaussian line width $\Delta H = 4.5$ G. b) The ESR-spectrum of the same sample after photo-bleaching at $\lambda > 515$ nm.

Fig. 2. ESR-spectrum of silica gel at 77°K in the dark after irradiation to a dose of 3.2 Mrad. The microwave power is kept at 0.01 mW.]
in which the intensities of the \( g = 2.0030 \), \( g = 2.0070 \), and \( g = 2.011 \) signals are lower than in the ordinary gel. Only very small amounts of deuterium atoms bleachable by visible light could be detected in a deuterated sample.

The spectrum from the silica gel sample prepared from silicon tetrachloride only differed significantly from that of the commercial gel after photobleaching. In this case the \( g = 2.011 \) signal was not observed.

Variation of the microwave power showed that the component at \( g = 2.0008 \) was saturated at the power level 1 mW usually applied. When the microwave power was lowered to 0.01 mW this line became the most predominant (Fig. 2) and contributed roughly 30 % to the integrated intensity. In these experiments the signal from the suprasil quartz sample tubes was annealed by heating in a torch before the measurements.

**Temperature effects.** When a silica gel sample was stored at 77°C for 55 days after irradiation the absorption intensity in the \( g = 2.0070 \) region decreased. The amplitudes of the \( g = 2.0008 \) and \( g = 2.0030 \) signals remained constant while the broad background signal approximately doubled its intensity. The signal strength of the \( g = 2.0070 \) absorption decayed almost com-

![Fig. 3. a) ESR-spectrum of silica gel irradiated and recorded at 300°C. The dose is 3.4 Mrad and the microwave power is of the order 50 mW. b) ESR-spectrum of silica-alumina irradiated and recorded at 77°C. The dose is 3.4 Mrad, and the microwave power is about 1 mW.](image)

![Fig. 4. a) The ESR signal recorded at 300°C and at a microwave power of about 1 mW from silica gel irradiated to a dose of 3.4 Mrad at 77°C. b) The spectrum obtained after air admission.](image)
pletely within 10 min at 160°K while the components at $g = 2.0030$ and $g = 2.008$ were more stable. At 300°K the absorption at $g = 2.0070$ had completely disappeared. The remaining signal was similar to a component in a sample irradiated at 300°K which could not be saturated (Fig. 3a). The broad spectrum having an envelope line width of about 35 G is centered at $g = 2.011$ and contains several peaks separated by 8G. The narrow line has $g = 2.0029$. The spectrum obtained from the silica-alumina gel (Fig. 3b) has a similar absorption at $g = 2.011$.

Reactions with adsorbed gases. The addition of air at 300°K to a silica gel sample which had previously been irradiated at 77°K and annealed at 300°K (Fig. 4a) gives a spectrum (Fig 4b) which may arise from species with an anisotropic $g$-tensor having the components $g = (2.025, 2.010, 2.003)$. When oxygen was adsorbed on a room temperature irradiated gel, essentially the same spectrum was observed. In these cases the reaction occurred within 30 min. The spectrum differs considerably from that obtained when a sample containing 1 % oxygen was irradiated at 77°K (Fig. 5). In the latter case the line shape is characteristic of an axially symmetric $g$-tensor having $g_\| = 2.0055 \pm 0.0005$, $g_\perp = 2.0037 \pm 0.0005$ and a Gaussian single line width $\Delta H = 4$ G, as seen by comparison with the calculated spectrum.

When a sample containing 3 % CO$_2$ was irradiated at 77°K to a dose of 3.4 Mrad a spectrum composed of the absorption at $g = 2.0070$ and a different species centered at $g = 2.0015$ (Fig. 6a) was recorded. After thermal annealing at 160°K for about 10 min only the latter signal remained (Fig. 6b). The line

*Fig. 5. ESR-spectrum from silica gel irritated in the presence of 1 % O$_2$ to a dose of 3.4 Mrad at 77°K. The dotted line represents a computed lineshape with the parameters $g_\|=2.0037$, $g_\bullet=2.0085$ and a Gaussian single crystal line width $\Delta H = 4$ G.*

*Fig. 6. ESR-spectrum from silica gel irritated in the presence of 3 % CO$_2$ to a dose of 3.4 Mrad at 77°K. a) at 77°K. b) after annealing at 160°K.*

shape indicates axial symmetry $g_{\perp} = 2.0024$, $g_{||} = 1.9971$. The radiation chemical yield of this species depends on the amount of CO$_2$ present. When a correction for the difference in temperature was applied it was found that the signal intensity remained unchanged after warming to 300°K. The number of radicals formed by 100 eV energy absorbed by the entire system, $G_{app}$, has been estimated as a function of the electron fraction $X_1$ of CO$_2$ present (Fig. 7). Within the limits of experimental error the $g = 2.0070$ signal has the same line shape and intensity as in the pure gel.

**DISCUSSION**

**Nature of Paramagnetic Centers**

The paramagnetic resonances observed in four-fold coordinated oxides have mostly been associated with defects which are either due to oxygen vacancies or to oxygen ions. The former types of defect serve as traps for electrons, while the paramagnetic states of oxygen ions act as trapped holes. Spin-orbit interaction makes the $g$-factors deviate from the free electron value $g_e = 2.0023$. However, as shown by Weeks, the electron traps may possess principal values $>g_e$, while for holes $g$-factors $<g_e$ can occur, in contrast to the usual expectation. In the absence of characteristic hyperfine structure the components must therefore be differentiated by other methods such as optical and thermal bleaching behaviour, microwave saturation properties and reactions with adsorbed species. Comparison with the results of previous investigators reveals a critical dependence of the type of gel used, sample degassing, influence of adsorbed gases, and temperature effects. Clearly, in order to make comparisons, it is necessary to take into account the differences in gel structure which may arise through the pretreatment and from the influence of impurities.

$g = 2.0008$ Component. A narrow easily saturated line around $g = 2.0010$ has previously been reported to appear in quartz single crystals and fused silica as well as in high surface area silica samples. This component is also present in irradiated hydrocarbon/silica gel systems. The absorption has been assigned to an electron trapped in an oxygen vacancy in the SiO$_2$ network.

It appears that the center is a bulk rather than a surface defect. This conclusion is supported by the observation that modification of the surface struc-
ture caused by the different heat treatments only slightly affects the signal intensity, by the insensitivity of line width to deuteration and by the lack of reactivity towards adsorbed gases.\textsuperscript{7b}

\[ g = 2.0030 \] Component. The line at \[ g = 2.0030 \], which at 3.4 Mrad constitutes 5 - 10% of the total absorption, seems to be associated with a centre localized to a limited number of traps since its contribution to the spectra becomes less at high doses. Wong and Willard\textsuperscript{6} observed a pronounced singlet at \[ g = 2.0028 \] in a silica gel under similar conditions. They suggested that the absorption may be caused by electrons trapped in voids of the type responsible for the trapping in glassy materials, which is not necessarily associated with oxygen vacancies. A singlet of this type seems to appear\textsuperscript{16} also in a silica gel free of impurities, indicating that it is not associated with the presence of iron or aluminium.

\[ g = 2.0070 \] Component. The absorption predominant before photobleaching (Fig. 1a) seems to be associated with a species with an axially symmetric \[ g \]-tensor \[ g_{\perp} = 2.0062 \], \[ g_{\|} = 2.0105 \]. Since the center is easily bleached and since the intensity depends markedly on the heat pretreatment it appears reasonable to suppose that it is localized to the surface. There are several indications that this resonance is caused by trapped holes. First, the presence of an electron scavenger such as carbon dioxide during the irradiation does not decrease the signal intensity. However, benzene completely quenches the formation of the \[ g = 2.0070 \] absorption and at the same time hydrocarbon cations are formed.\textsuperscript{13} In the presence of hexane a gradual decrease of the intensity with increasing alkane content takes place. Secondly, the signal does not saturate easily at increased microwave power. Finally, the resonances observed from trapped electrons in irradiated quartz\textsuperscript{17} are located at \[ g < g_{c} \].

The optical bleaching at \( \lambda > 1000 \) nm may occur through an electron transition from an electron trap. The upper limit of the energy required to make the electron mobile is then 1.25 eV. The electron traps seem to be different from those detected by their resonance absorption since the latter signals disappear less readily upon optical or thermal bleaching than the \( g = 2.0070 \) center.

The formation of holes associated with molecular oxygen ions appears less likely following irradiation of the evacuated samples. For \( O^- \) in a crystal field with axial symmetry, the situation \( g_{\perp} > g_{\|} \), \( g_{\parallel} = g_{c} \) is to be expected.\textsuperscript{2} In the \( MO^- \) type of center studied in alkali glasses, however, the observation \( g_{\perp} < g_{\|} \) was made (cf. Ref. 2). This may be due to a change of the relative ordering of the energy levels in the molecular orbitals of \( MO^- \) compared to those of \( O^- \) in conjunction with a lower (rhombic) symmetry\textsuperscript{2} of the crystal field. As the silica gel contains no glass-modifying cations, the formation of non-bridging oxygens of the type observed in the alkali silicate glasses\textsuperscript{2} must be of minor importance. In the silica gel a hole centered at a non-bridging oxygen may be formed by the rupture of an \( O-H \) bond in a surface silanol group. The assignment of the observed signal to such a species is supported by the observation that an electron scavenger like carbon dioxide does not affect the intensity of the absorption. Centers formed by electron loss show an increased stability under these conditions due to the trapping of electrons which could otherwise recombine with the holes.\textsuperscript{19} A non-bridging oxygen attached to a surface aluminium ion seems to be ruled out as the centre also dominates

in the synthesized sample. A species with similar properties has been detected in boron containing silica,\cite{18} in which case the hole was considered to be localized mainly on the 2s and 2p orbitals of a non-bridging oxygen next to a boron atom, giving hyperfine interaction. In this case \( g_\parallel = 2.0100 \) and \( g_\perp = 2.0023 \) was observed being consistent with the theoretical model proposed.

The low intensity of the absorption in samples preheated at 350°C may be due to adsorbed water which is known\cite{30} to prohibit the formation of this species.

\( g = 2.011 \) Component. The spectrum at 77°C remaining after photobleaching, in which a structure is barely resolved (Fig. 1b), is probably of the same origin as the broad signal at \( g = 2.011 \) observed after room temperature irradiation of silica gel (Fig. 3a). An analogous absorption has also been reported in fused quartz irradiated with neutrons.\cite{31} This spectrum, which had a width of about 50 G, was assigned to a center showing hyperfine interaction with the \( ^{27}\text{Al} \) nucleus present as an impurity. Similar defects have been observed in smoky quartz, and a theoretical model has been proposed\cite{32} to explain the parameters \( g_\parallel = 2.06 \), \( g_\perp = 2.00 \), \( A_\perp = 5.1 \) G, \( A_\parallel = A_\perp = 6.0 \) G. Although it seems very likely that the observed splittings are caused by \( ^{27}\text{Al} \) hyperfine interaction, these parameters do not fit the experimental spectrum. According to Vedrine \textit{et al.}\cite{33} in silica-alumina two centers \( V_1 \) and \( V_2 \) account for the broad background signal. These are attributed to holes trapped at non-bridging oxygens bonded to trigonally coordinated aluminium ions. The resolved structure is caused by a hole trapped on an oxygen atom in an \( \text{AlO}_4 \) unit. Although the detailed interpretation of Vedrine \textit{et al.} is not conclusive, the close similarity between the spectra from silica alumina and that from silica gel (Fig. 1, 3) gives strong evidence for the formation of hole centers associated with aluminium ions present as an impurity. Further evidence for the assignment is that the absorption intensity was reduced in an acid treated gel and was not observed in the synthesized gel.

The apparent increase in intensity upon storage at 77°C has been attributed to a line narrowing caused by an increased ordering of the crystal structure.\cite{3} Possibly also a transformation of the \( g = 2.0070 \) line into the \( g = 2.011 \) signal has occurred.

\textbf{Paramagnetic centers in the presence of electron scavengers}

Electron transfer between molecules having high electron affinity such as \( \text{O}_2 \), \( \text{N}_2\text{O} \), \( \text{CO}_2 \) and electron sites in the irradiated silica,\cite{6,7,11} silica-alumina\cite{24} and magnesium oxides\cite{25} has been observed in several instances. The identification of \( \text{O}_2^- \) by its \( g \)-tensor may be ambiguous since the principal values depend on the matrix (cf. Ref. 2). This also holds true for \( \text{O}^- \), which is formed by dissociative electron attachment\cite{26} to \( \text{N}_2\text{O} \). On the other hand the \( \text{CO}_2^- \) radical has been unambiguously identified by its \( g \)-tensor and \( ^{13}\text{C} \) splitting.\cite{7} Evidence for electron migration during irradiation\cite{11} was obtained with the use of scavengers such as galvinoxyl, alkyl halides, biphenyl and naphthalene.

\textit{Oxygen}. The change in spectral appearance when oxygen is admitted at room temperature by the reaction with trapped electrons in the preirradiated silica gel (Fig. 4) has been attributed to the formation of \( \text{O}_2^- \) ions.\cite{5} Centers of

this type are also formed by the reaction with electrons in silica-alumina.24
A similar reaction has been observed on a pre-irradiated MgO surface.25 The
formation of O$_2^-$ rather than O$^-$ was inferred from the $^{17}$O hyperfine splitting
and is also favoured on energetic grounds.24

The resonance observed from silica gel irradiated at 77$^\circ$K in the presence
of oxygen (Fig. 5) has previously been reported by Kohn.27 As judged from the
g-factors the absorption may be caused by centers of the type O$^-$ and MO$^-$,
similar to those found in the pure gel. The rate of formation of these centers
would then be increased considerably in the presence of oxygen, $G=1.2$
molecules/100 eV compared to $G=0.25$ at the same dose, 3.4 Mrad, in the
silica gel. This agrees with the suggestion of Hentz and Wickenden19 that O$_2$
and N$_2$O act as traps for free electrons and enhance the positive hole signal of
silica-alumina. Another reasonable explanation is that centers of the type O$^-$
and MO$^-$ are formed from the condensed gases. Due to this difficulty in the
interpretation, the use of CO$_2$ as an electron scavenger seemed more
advantageous and was chosen for a quantitative study.

Carbon dioxide. The species observed (Fig. 6) has an axial g-tensor
$g_0=1.9971$, $g_1=2.0024$ in close agreement with the parameters observed for
CO$_2^-$ in the silica gel/carbon dioxide system during UV irradiation.7 In the
adsorbed state the small difference between the largest components of the g-
tensor is not resolved, and similarly the $^{13}$C structure can only be observed in
$^{12}$C enriched samples.7b

**Reactivity of the gel**

The radiation induced reactions on the surface of silica gel has been in-
vestigated in the presence of molecules known as electron scavengers11 and
with olefins8 and aromatic compounds13,28 which could accept hydrogen atoms
and also become ionized. It appears that three different types of transfer
reaction take place, namely electron transfer, positive charge transfer, and
hydrogen atom transfer from the silica gel to the adsorbed molecules. Evidence
for the two last reactions was presented previously15 and will not be discussed
here.

**Electron transfer.** The deviation from linearity when $G_{app}$ is plotted against
$X_1$, the electron fraction of adsorbed molecules, has previously been noted in
hydrocarbon/silica gel systems.12,13 This behaviour is indicative of some interac-
tion between the phases, and it was suggested that energy was transferred12
from the gel to the adsorbed molecules.

The present results (Fig. 7) suggest that electrons originally liberated in the
gel become trapped at carbon dioxide molecules to yield CO$_2^-$ . This may occur
at a limited number of sites with a yield $G_{ads}$. From a previously proposed
model12 and the data of Fig. 7 a least squares fit yields $G_{ads}=2.1 \pm 0.8$,
$X_1^2=0.037 \pm 0.08$. The errors given are twice the standard deviations. $X_1^2$
is the electron fraction of carbon dioxide when all sites are saturated and the
value found corresponds to a distance of about 1.0 nm between the molecules.
An electron originally created in the interior of the gel must be transferred
to the surface before it can react with the adsorbed molecules. This distance
can be estimated from the surface area to be of the order 1.5 nm. At lower

coverage the probability of CO$_3^-$ ion formation is decreased since the electron must travel a longer path and can then become stabilized at other traps or escape. In scavenger experiments using galvinoyxl the yield of electrons was considerably higher, demonstrating that not all of the radiolytically liberated electrons become trapped as CO$_3^-$ This gives further evidence that only a limited number of sites are available for CO$_3^-$ formation.

CONCLUSIONS

In discussing the paramagnetic species induced in silica gel by $\gamma$-irradiation it seems necessary to take into account the differences in gel structure caused by various pretreatments and by impurities. Further, the absence of hyperfine structure and the uncertainty in the interpretation of the shift of the $g$-factor values from that of the free electron makes it necessary to differentiate the species by their optical and thermal bleaching properties.

The assignment of the $g = 2.0008$ absorption, which constitutes about 30% of the total absorption, to an electron trapped at an oxygen vacancy site and as a bulk property of the silica gel seems very well supported. The $g = 2.0030$ absorption appears in a smaller amount and it also saturates quantitatively at higher doses. No unambiguous assignment can be made on the basis of the evidence at present available, but the species are probably due to electrons trapped in a limited number of sites.

The identification of the $g = 2.0070$ absorption as a hole center trapped on the surface of the silica gel seems very plausible. However, its detailed structure is still unclear, but the hole is most probably located near to a non-bridging oxygen atom. The center at $g = 2.011$ is also attributed to a hole, which is located close to a $^{27}$Al nucleus. An apparent increase in intensity upon storage indicates a line narrowing due to increased order of the matrix or to a turnover of the first hole center into the second one.

The study of the influence of adsorbed molecules on the formation of the centers gives evidence for three types of transfer reactions, i.e. firstly, transfer of electrons from the interior of the gel to the surface, where they attach to electron scavenging molecules, secondly, hole transfer, which occurs with varying efficiency depending upon the trapping ability of the adsorbate, and thirdly, transfer of hydrogen atoms.

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