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Free Radicals and Reactive Molecules in Clathrate Cavities

Abstract. *Reactive molecules and free radicals, when located in the cavities of the water clathrate lattice, can be prevented from recombining at temperatures almost up to the decomposition point of the lattice. The active species are produced by selective photochemical dissociation of the guest molecules in the clathrate compounds. Data taken from water clathrates of H₂S, CH₃SH, and C₂H₅SH suggest that S₂, CH₃S and C₂H₅S can be preserved in this way.*

At present the long-term stabilization of reactive small molecules and free radicals in solid matrices requires low temperatures, often below 77°K (1). It is thus of general interest to devise means for stabilizing such reactive species at higher temperatures to facilitate study and use. The unique properties of the clathrate lattice offer a possible solution. Clathrates are well-defined crystalline materials of two components, the *host*, which forms the lattice framework in which cavities exist, and the *guest*, which is located in the cavities (2). There is no primary chemical bonding between the guest and the host. The possibility of using clathrates to stabilize free radicals has been mentioned by Peiser (3) and Rice (4). No work has thus far been reported, although the studies of Griffith and McConnell on x-irradiation of in-

clusion compounds of urea bear upon the problem (5).

The clathrate lattice can be used for stabilization of reactive species. The theoretical considerations are the following. The guest, *MH*, is a photosensitive compound which dissociates to yield a hydrogen atom and a larger fragment, *M*. Reactions of the type $MH \rightarrow M + H$ and $H + MH \rightarrow H_2 + M$ will occur since H and H₂ are mobile and can overcome the cage effect. *M* may also be mobile, depending on its size and kinetic energy after dissociation. If *M* is mobile, then $M + M \rightarrow$ (products) will occur. Alternatively, if *M* cannot move it will remain in its cage, unable to recombine so long as the lattice is stable.

Experimentally, water was chosen as the host because of its photochemical stability and optical properties.

H₂S, CH₃SH, and C₂H₅SH were used as photosensitive guests in the following single and double clathrates of water: H₂S, (CH₂Cl₂, H₂S), (CHCl₃, H₂S), (CCl₄, H₂S), CH₃SH, and (C₂H₅SH, Ar). Also the double water clathrate (CHCl₃, Ar) was prepared. In all cases the materials were of snow-like consistency. This required that their spectral properties be recorded by diffuse reflectance spectroscopy, which was done at -80°C with a special reflectance attachment. The photodecompositions were effected at -80°C (the 2537-Å Hg line was used). In addition, CH₃SH was photolyzed in a polar organic glass at liquid air temperature.

In the case of the water clathrate of CH₃SH irradiation produces a strong absorption at $\lambda_{max} = 370 m\mu$ with a shoulder at 310 $m\mu$. Absorption also increases in the range 0.8 to 2.0 μ due to irradiation, but no maximum is observed. A similar spectrum obtains with (C₂H₅SH, Ar) water clathrate. The ultraviolet absorption diminishes after the irradiated material is allowed to decompose partially by warming. Spectra taken at -80°C after progressive partial annihilation evolve to the same shape as the spectrum of the unirradiated material. Photolysis of CH₃SH in the organic glass leads to a yellow coloration and an absorption maximum at 400 $m\mu$ as measured in transmission. The yellow color disappears when the glass is melted.

The reflectance spectrum of the (CHCl₃, Ar) water clathrate is structureless before and after ultraviolet irradiation.

Figure 1 shows the reflectance spectra of the water clathrate of H₂S before and after irradiation. Reflectance is plotted downward to give the curves the aspect of absorption. In the unirradiated material the strong absorption beginning at 280 $m\mu$ and increasing toward shorter λ is that of H₂S. The irradiated sample shows a strong, broad band with $\lambda_{max} = 280$ to 290 $m\mu$ and a weaker one in the visible at $\lambda_{max} = 560 m\mu$, which imparts a purple color to the sample. The other maximum, at 250 $m\mu$, is also present before irradiation in other experiments and must be attributed to H₂S. The spectra of all the double clathrates of H₂S are identical with one another and are similar to those shown in Fig. 1 except that the visible band is narrower in width and the maximum is displaced to 520 $m\mu$. The double clathrates are pinkish-purple after irra-

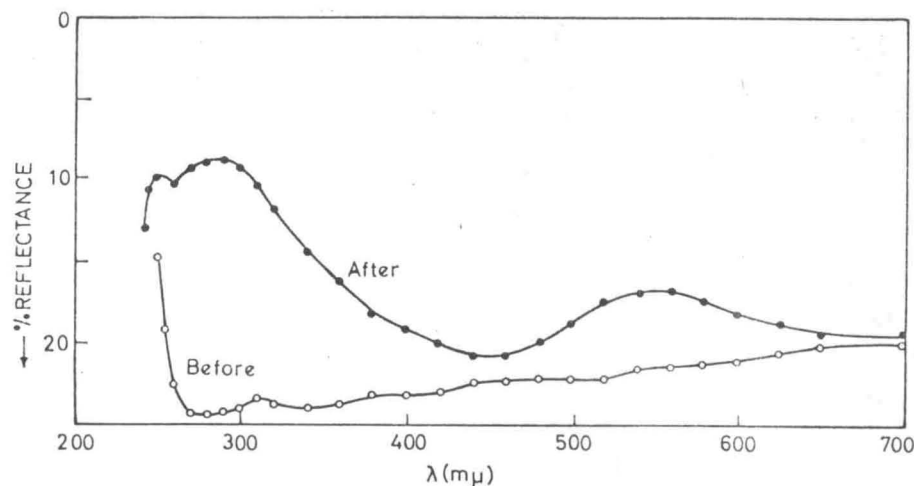


Fig. 1. Reflectance spectra of the H₂S clathrate of water before and after irradiation. MgCO₃ used as reference reflectance standard. Lamp to sample distance, 2.9 cm; source, 140-watt low-pressure Hg lamp (filtered with 0.1M NaCl solution); irradiation time, 15 minutes at -80°C.

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As previously reported in the following
 and similar studies of water,
 H₂O, CH₃OH, H₂N, CO₂, H₂S,
 H₂CO, H₂, CH₄, and C₂H₆.
 Also the double water molecule
 (H₂O)₂ was present. In all cases
 the material was in equilibrium with
 water. This showed that they were
 not completely frozen by dilution
 of the polymer solution by dilution
 with water. The infrared which was
 done at 20°C with a special reflector
 and detector. The observations
 shown were obtained at 20°C. The
 H₂O and H₂ lines were used in the
 H₂O and H₂ was prepared in a
 special way in order to be prepared
 in the case of the water molecule
 of H₂O. The infrared shows a strong
 absorption at 3700 cm⁻¹ and with
 a shoulder at 3100 cm⁻¹. Absorption
 bands at 3700 cm⁻¹ and at 3100
 cm⁻¹ are characteristic of hydrogen
 and to hydrogen and to hydrogen
 bonds. The infrared spectrum of
 the pure water (H₂O) water shows
 the infrared absorption bands
 which after the previous material
 is allowed to evaporate partially by
 warming slightly from 20°C
 after progressive partial condensation
 under the same steps as the step
 from of the condensed material. The
 bands of H₂O in the infrared
 look to a rather common and an
 absorption maximum at 4000 cm⁻¹
 is observed in condensed water. The
 color is observed when the glass is
 given.

The infrared spectrum of the
 (H₂O) water shows a strong
 band at 3700 cm⁻¹ and at 3100
 cm⁻¹. The infrared spectrum of
 Figure 1 shows the infrared spec-
 tra of the water molecule of H₂O
 and after dilution. The infrared
 bands shown in the figure are
 a rather strong and give the color
 of absorption in the
 infrared region. The infrared spec-
 tra obtained at 20°C and at 20°C
 are shown in Figure 1. The
 infrared bands shown are
 the infrared bands with $\lambda = 2.9$ to 3.0
 μ and a weaker one in the visible
 at $\lambda = 700$ m μ . The infrared
 a purple color in the infrared. The
 infrared maximum at 3700 cm⁻¹
 given below and at 3100 cm⁻¹
 present and must be attributed to
 H₂O. The spectra of all the bands
 characteristic of H₂O are identical with
 another and are similar to those
 in Fig. 1 except that the visible
 is covered in white and the maximum
 is displaced to 710 m μ . The infrared
 changes in purple-purple after the

Free Radicals and Reactive Interiors in Chlorine Latex

Abstract. Reaction products and free radicals in the interior of the water swollen latex can be observed from measurements on...
 about up to the breaking point of the latex. The active radicals are
 found to be in equilibrium with the monomer of the latex. The
 chlorine compounds are also found to be in equilibrium with the
 Cl₂ molecules and to be in equilibrium with the latex.

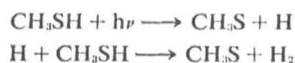
At present the investigation is a
 of reaction products and free
 radicals in the interior of the
 emulsion, after the reaction
 of the water swollen latex to
 a solid state. The reaction
 products are observed from
 measurements on the
 infrared spectrum of the
 latex. The infrared spectrum
 shows a strong absorption
 band at 3700 cm⁻¹ and at
 3100 cm⁻¹. The infrared
 spectrum of the pure water
 shows a strong absorption
 band at 3700 cm⁻¹ and at
 3100 cm⁻¹. The infrared
 spectrum of the water
 molecule of H₂O and after
 dilution. The infrared
 bands shown in the figure
 are a rather strong and
 give the color of absorption
 in the infrared region. The
 infrared spectra obtained
 at 20°C and at 20°C are
 shown in Figure 1. The
 infrared bands shown are
 the infrared bands with
 $\lambda = 2.9$ to 3.0 μ and a
 weaker one in the visible
 at $\lambda = 700$ m μ . The
 infrared a purple color
 in the infrared. The
 infrared maximum at
 3700 cm⁻¹ given below
 and at 3100 cm⁻¹ present
 and must be attributed
 to H₂O. The spectra of
 all the bands characteristic
 of H₂O are identical
 with another and are
 similar to those in
 Fig. 1 except that the
 visible is covered in
 white and the maximum
 is displaced to 710 m μ .
 The infrared changes
 in purple-purple after
 the



Fig. 1. Infrared spectrum of the H₂O molecule of water and after dilution.
 The infrared bands shown are the infrared bands with $\lambda = 2.9$ to 3.0 μ and a
 weaker one in the visible at $\lambda = 700$ m μ . The infrared a purple color
 in the infrared. The infrared maximum at 3700 cm⁻¹ given below
 and at 3100 cm⁻¹ present and must be attributed to H₂O. The spectra
 of all the bands characteristic of H₂O are identical with another
 and are similar to those in Fig. 1 except that the visible is covered
 in white and the maximum is displaced to 710 m μ . The infrared
 changes in purple-purple after the

diation. The ultraviolet (280 to 290 $m\mu$) and visible bands grow parallelly, suggesting that the two bands arise from the same species. The color is stable for at least 3 to 5 hours at -80°C . Though fading is apparent at higher temperatures, color is still detectable after 45 minutes at -20°C . In experiments with the water clathrate of $(\text{CCl}_4, \text{H}_2\text{S})$ color develops with the sample held between -10° and -2°C during irradiation. Color stability here is the order of 1 or 2 minutes.

These observations can be interpreted in terms of reactive species located in cavities of the water clathrate. In the CH_3SH clathrate CH_3S is assumed to be stabilized. This is produced by the following reactions (6):

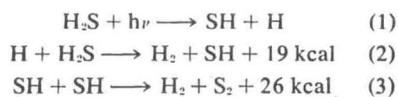


Similarly, $\text{C}_2\text{H}_5\text{S}$ resides in the cavities of its parent clathrate. Evidence in support of these assignments comes from the work of Rosengren, who shows that photolysis of mercaptans in hydrocarbon glasses at 77°K produces absorptions with λ_{max} at 400 $m\mu$ which are assigned to RS radicals (7). My experiments in polar glass with CH_3SH provide independent confirmation of Rosengren's results.

The observed temperature stability of the absorption bands reinforces the hypothesis that the radicals occupy clathrate cavities. Though diminished in intensity, the 310- and 370- $m\mu$ bands survive annealing at -20°C for 40 minutes.

It is not likely that CH_3S and $\text{C}_2\text{H}_5\text{S}$ will disproportionate in their cavities. The absorptions assigned here to these radicals are unlike those reported for products of thiyl radical disproportionation (8).

In the H_2S clathrates the stabilized species is assumed to be S_2 . This is produced by the following reactions (9):



The radius of escape from the cavities varies from 1.0 to 1.5 \AA , depending on cavity size (10). SH is too large (radius = 1.7 \AA) to diffuse interstitially. After dissociation, however, the products possess sufficient kinetic energy to distort the hydrogen bonded lattice, permitting SH to pass from the parent cage into a neighboring one and to react according to reaction 3 (11). Evidence in support of S_2 , one of the

known products of photolyzed H_2S , as the absorbing species in Fig. 1 is drawn from (i) the maximum in the ultraviolet absorption of Fig. 1 at 280 to 290 $m\mu$ which falls near the position of the strongest absorption bands of the ν', ν progression of S_2 (12) and (ii) the absorption band with $\lambda_{\text{max}} = 507 m\mu$ reported in low temperature deposits of S_2 (13). This band falls reasonably close to the 520 and 560 $m\mu$ bands of the water clathrates of H_2S . Higher polymers of sulfur (for example, S_8 and S_x) can probably be ruled out of consideration because their absorption characteristics (14) do not fully satisfy both i and ii.

The stability of color at relatively high temperatures also supports the view that the active species is stabilized in the cavities.

The spectral differences between the single and double water clathrates of H_2S may originate in structural differences between the hydrate types. Single hydrates all form in a cubic lattice of 12 \AA unit cell edge with two sizes of cavity: 5.2 \AA and 5.9 \AA free diameters. The double hydrates form also in a cubic symmetry, of unit cell edge 17.3 \AA , again with two sizes of cavity: 4.8 \AA and 6.9 \AA (15). Thus S_2 resides in a cavity of different size according to the structure of the water clathrate from which it was formed. Consequently the S_2 energy levels experience a matrix shift relative to the gas phase spectrum, the magnitude of shift depending on cavity size. Concentrations of stabilized species cannot be given at the present time (16).

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- The radii of CH_3S and $\text{C}_2\text{H}_5\text{S}$ are estimated to be 2.4 and 3.1 \AA , respectively. These radicals are probably too large to move from

their parent cages by the mechanism proposed for SH.

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