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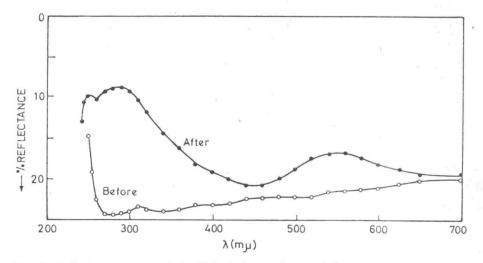
Free Radicals and Reactive Molecules in Clathrate Cavities

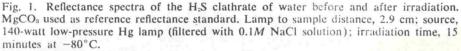
Abstract. Reactive molecules and free radicals, when located in the cavities of the water clathrate lattice, can be prevented from recombining at temperatures almost up to the decomposition point of the lattice. The active species are produced by selective photochemical dissociation of the guest molecules in the clathrate compounds. Data taken from water clathrates of H_2S , CH_2SH , and C_2H_2SH suggest that S_2 , CH_2S and C_2H_2S 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 welldefined 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 inclusion 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 H. 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.





H.S., CH.SH, and C.H.SH were used as photosensitive guests in the following single and double clathrates of water: H:S, (CH:Cl:, H:S), (CHCl:, H:S), (CCl₄, H₂S), CH₃SH, and (C₂H₅SH, Ar). Also the double water clathrate (CHCl_a,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-A 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 of CH-SH irradiation produces a strong absorption at $\lambda_{max} = 370 \text{ m}\mu$ with a shoulder at 310 mµ. 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 (C4HaSH,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 CH-SH in the organic glass leads to a yellow coloration and an absorption maximum at 400 m μ as measured in transmission. The yellow color disappears when the glass is melted.

The reflectance spectrum of the (CHCl_a,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 μ and increasing toward shorter λ is that of H.S. The irradiated sample shows a strong, broad band with $\lambda_{max} = 280$ to 290 $m\mu$ and a weaker one in the visible at $\lambda_{max} = 560 \text{ m}\mu$, which imparts a purple color to the sample. The other maximum, at 250 mµ, is also present before irradiation in other experiments and must be attributed to H₂S. The spectra of all the double clathrates of H:S 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 mµ. The double clathrates are pinkish-purple after irra-

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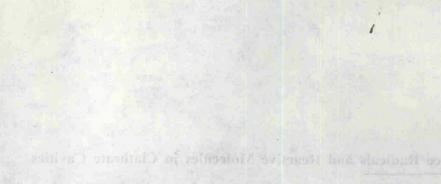
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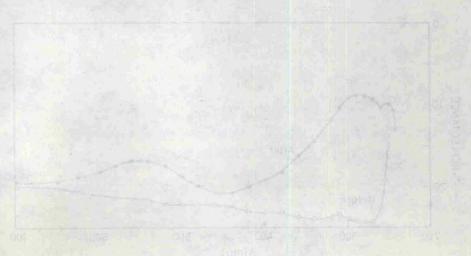
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diation. The ultraviolet (280 to 290 m_{μ}) and visible bands grow parallelly, suggesting that, the two bands arise from the same species. The color is stable for at least 3 to 5 hours at -80°C. Though fading is apparent at higher temperatures, color is still detectable after 45 minutes at -20° C. In experiments with the water clathrate of (CCl₁, H₂S) color develops with the sample held between -10° and $-2^{\circ}C$ 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 CH₃SH clathrate CH₃S is assumed to be stabilized. This is produced by the following reactions (6):

> $CH_3SH + h_{\nu} \longrightarrow CH_3S + H$ $H + CH_3SH \longrightarrow CH_3S + H_2$

Similarly, C2H5S 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 μ which are assigned to RS radicals (7). My experiments in polar glass with CHaSH 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 μ bands survive annealing at -20° C for 40 minutes.

It is not likely that CH₃S and C₂H₅S 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 H₂S clathrates the stabilized species is assumed to be S2. This is produced by the following reactions (9):

$H_2S + h_P \longrightarrow SH + H$	(1)
$H + H_2S \longrightarrow H_2 + SH + 19$ kcal	(2)
$SH + SH \longrightarrow H_2 + S_2 + 26$ kcal	(3)

The radius of escape from the cavities varies from 1.0 to 1.5 Å, depending on cavity size (10). SH is too large (radius = 1.7 Å) 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 S2, one of the

known products of photolyzed H₂S, 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 v',o progression of S_2 (12) and (ii) the absorption band with $\lambda_{max} = 507 \text{ m}\mu$ reported in low temperature deposits of S_2 (13). This band falls reasonably close to the 520 and 560 m μ bands of the water clathrates of H2S. Higher polymers of sulfur (for example, Sa and S_{*}) 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 H₂S may originate in structural differences between the hydrate types. Single hydrates all form in a cubic lattice of 12 Å unit cell edge with two sizes of cavity: 5.2 Å and 5.9 Å free diameters. The double hydrates form also in a cubic symmetry, of unit cell edge 17.3 Å, again with two sizes of cavity: 4.8 Å and 6.9 Å (15). Thus S2 resides in a cavity of different size according to the structure of the water clathrate from which it was formed. Consequently the S₂ 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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