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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-

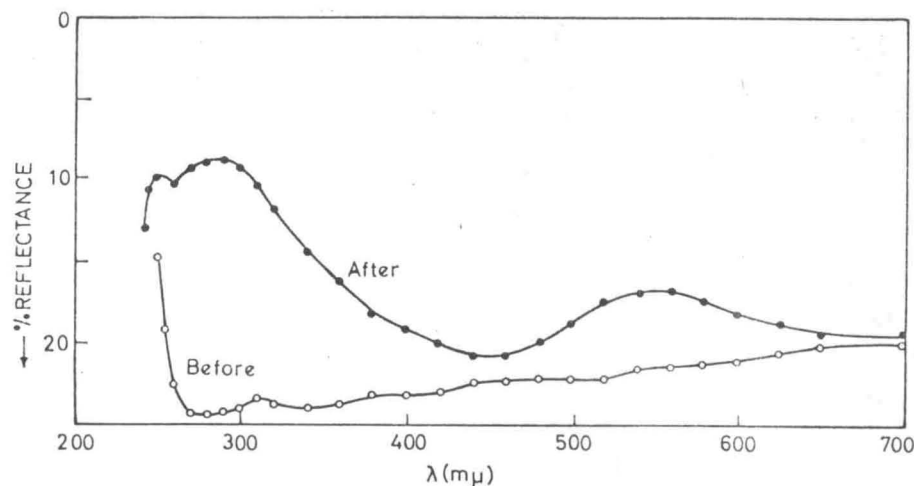


Fig. 1. Reflectance spectra of the H₂S clathrate of water before and after irradiation. MgCO₃ used as reference reflectance standard. Lamp to sample distance, 2.9 cm; source, 140-watt low-pressure Hg lamp (filtered with 0.1M NaCl solution); irradiation time, 15 minutes at -80°C.

