Reports

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_3SH, and C_2H_5SH suggest that S_2, CH_3S and C_2H_5S 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 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_2 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_2S, CH_3SH, and C_2H_5SH were used as photosensitive guests in the following single and double clathrates of water: H_2S, (CH_2Cl_2, H_2S), ($CHCl_3$, H_2S), (CCl_4, H_2S), CH_3SH, and (C_2H_5SH, Ar). Also the double water clathrate ($CHCl_3$,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, CH_3SH was photolyzed in a polar organic glass at liquid air temperature.

In the case of the water clathrate of of CH_3SH irradiation produces a strong absorption at $\lambda_{max} = 370$ mμ 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 (C_2H_5SH,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_3SH in the organic glass leads to a yellow coloration and an absorption maximum at 400 mμ as measured in transmission. The yellow color disappears when the glass is melted.

The reflectance spectrum of the ($CHCl_3$,Ar) water clathrate is structureless before and after ultraviolet irradiation.

Figure 1 shows the reflectance spectra of the water clathrate of H_2S 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 mμ and increasing toward shorter λ is that of H_2S. The irradiated sample shows a strong, broad band with $\lambda_{max} = 280$ to 290 mμ and a weaker one in the visible at $\lambda_{max} = 560$ mμ, 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 H_2S. The spectra of all the double clathrates of H_2S 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-

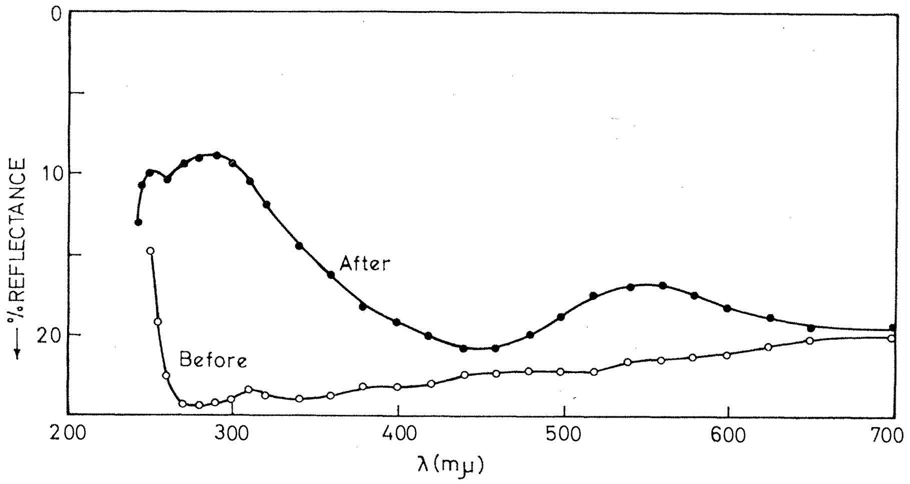

Fig. 1. Reflectance spectra of the H_2S clathrate of water before and after irradiation. $MgCO_3$ used as reference reflectance standard. Lamp to sample distance, 2.9 cm; source, 140-watt low-pressure Hg lamp (filtered with 0.1M NaCl solution); irradiation time, 15 minutes at −80°C.

diation. The ultraviolet (280 to 290 mμ) 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 (CCl_4, H_2S) 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*):

$$CH_3SH + h\nu \longrightarrow CH_3S + H$$

$$H + CH_3SH \longrightarrow CH_3S + H_2$$

Similarly, C_2H_5S 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 mμ 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-mμ bands survive annealing at −20°C for 40 minutes.

It is not likely that CH_3S and C_2H_5S 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*):

$$H_2S + h\nu \longrightarrow SH + H \tag{1}$$

$$H + H_2S \longrightarrow H_2 + SH + 19\ \text{kcal} \tag{2}$$

$$SH + SH \longrightarrow H_2 + S_2 + 26\ \text{kcal} \tag{3}$$

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 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 mμ 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 $\lambda_{max} = 507$ mμ reported in low temperature deposits of S_2 (*13*). This band falls reasonably close to the 520 and 560 mμ bands of the water clathrates of H_2S. Higher polymers of sulfur (for example, S_6 and S_8) 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 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 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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References and Notes

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Coesite and Shocked Quartz from Holleford Crater, Ontario, Canada

Abstract. *The Holleford Crater, a circular depression in southern Ontario, is filled with Paleozoic sediments and underlain by brecciated Precambrian igneous and metamorphic rocks. The presence of coesite in two core samples of this breccia has been established by petrographic and x-ray diffraction methods. Shattered quartz in the coesite-bearing samples exhibits planar fractures. The shocked quartz is the result of great shock pressures and the association of coesite with the shocked quartz strongly suggests that Holleford Crater originated from a hypervelocity impact.*

Holleford Crater is located approximately 25.7 km. (16 mi) north of Kingston, and 132 km (82 mi) southwest of Ottawa, Ontario, Canada (*1*). This circular depression was first recognized by Beals, Ferguson, and Landau in a systematic search of aerial photographs of various regions in Canada (*2*). In 1956–57, Beals directed a comprehensive study of the crater by geological and geophysical methods. This study included drilling three diamond drill holes that successively penetrated Paleozoic limestone, consolidated breccia, and Precambrian plutonic rocks, as described by Beals (*2*) who made available the core samples used in this investigation. The crater, 2.35 km (1.46 mi) in diameter and 30.5 m (100 ft) deep, is in Precambrian rock. Several hundred feet of breccia lies in a bowl-shaped depression in the Precambrian rock surface and is overlain by Paleozoic sediments. Beals estimates the age of the crater