

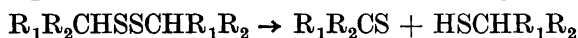
The Photolysis of Alkanethiols in a Rigid Glass at 77° K with the Possible Formation of Thiyl Radicals

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The photolysis of ethanethiol, 2-propanethiol and 1-butanethiol in an organic matrix at 77°K leads to the formation of a rather sharp and fairly stable absorption peak at about 25 kc. cm^{-1} . After warm-up to room temperature, considerable quantities of disulfide were found in the solution. From this and additional experimental evidence, it is concluded that this peak best can be assigned to the thiyl radical.

It has been repeatedly suggested that UV-irradiation of a disulfide leads to the formation of intermediate thiyl radicals (for the literature see, *e.g.*, Ref. ¹). In an attempt to trap thiyl radicals by photolysis in an organic matrix at liquid nitrogen temperature it has been demonstrated that no such trapping occurred as could be detected by UV-spectrophotometry ¹. As an explanation it has been suggested that the negative result is due to the cage-effect (Ref. ², p. ⁹⁵) that is, the excited thiyl radicals formed in the initial chemical process were unable to separate and therefore reacted according to



where R = H or Alk.

Porter *et al.* ^{3,4} have reported the successful trapping of a number of radical species by the photolysis reaction $\text{RXH} \rightarrow \text{RX}\cdot + \text{H}$ utilizing the fact that hydrogen atoms easily diffuse through the organic matrix even at 77°K. Consequently, photolysis of an alkane thiol might lead to the desired result — formation of a thiyl radical.

RESULTS

The apparatus and technique used have been described elsewhere ^{5,6}. Ethanethiol, 2-propanethiol and 1-butanethiol, all of satisfactory purity as judged from GLC, were used in the experiments. Isopentane and 3-methyl

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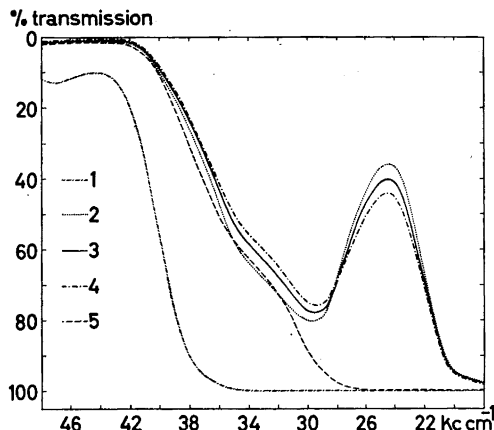


Fig. 1. Photolysis of *n*-BuSH in the matrix. (1) before photolysis at 77°K, (2) immediately after 10 min of photolysis, (3) 30 and (4) 60 min after the end of photolysis. (5) at 298°K.

pentane, 6:1, were used as a matrix-forming mixture. The primary and secondary mercaptans exhibit a weak UV-absorption (ϵ ca. 150) at 43 kc. cm^{-1} ; for 0.05 and 5 mM solution the transmission is 100 % below 40 and 34 kc. cm^{-1} , respectively. In the paper cited¹, control photolyses were performed on 0.4 mM 1-butanethiol using WG7 filters. The main change in spectrum during photolysis was a pronounced *increase* in transmission between 50 and 46 kc. cm^{-1} . However, when the photolysis was carried out on 5 mM solutions, all other conditions being equal, the results were as given in Fig. 1. Curve 1 shows the spectrum at 77°K before photolysis. Curve 2 was recorded immediately after 10 min of irradiation. When the sample cell was left at 77°K, curves 3 and 4 were recorded after 30 and 60 min, respectively.

The decrease of the 24.6 kc. cm^{-1} peak is evident as is the formation of an isosbestic point at 28 kc. cm^{-1} . When the irradiation was prolonged no further increase of the peak occurred, probably because the increase in ultraviolet absorption above 30 kc. cm^{-1} prevented further photolysis of the mercaptan molecules.

When the cells were lifted up from the liquid nitrogen an uneven distribution of the yellow color (24.6 kc. cm^{-1} peak) was observed, the layers near the windows being most strongly colored. The color disappeared when the cell content lost its rigidity and no traces of the peak could be seen at room temperature (curve 5); nor did it appear again when the sample was cooled in liquid nitrogen for a second time. Similar experiments performed with ethanethiol and 2-propanethiol gave analogous results, the absorption peak occurring at 25.6 and 24.8 kc. cm^{-1} , respectively.

The following experiment was performed to show the existence of thiyl radicals in the photolyzed glass. A 5 mM ethanethiol solution photolyzed at 77°K was evaporated slightly above room temperature under a stream of nitrogen. An equal amount of the unphotolyzed solution was treated in exactly

the same way. After the solution had been reduced to about a hundredth of the initial volume, samples were withdrawn, put on the gas chromatograph and analyzed for ethyl disulfide. The photolyzed sample gave a large disulfide peak, whereas it was totally absent in the control experiment.

DISCUSSION

The experimental results strongly indicate that the 24.6 kc. cm^{-1} peak should be assigned to the butylthiyl radical. It is commonly supposed that larger molecular species do not migrate in the hydrocarbon glasses at 77°K (Ref. ², p. 78) and moreover in the preceding paper it was shown that no mixed disulfide was formed at 77°K when a mixture of two alkyl disulfides was photolyzed. Therefore, it can safely be assumed that disulfide cannot be formed in considerable amounts at 77°K by photolysis of a mercaptan. The correspondence between the irreversible disappearance of the 24.6 kc. cm^{-1} peak during warm-up and the simultaneous formation of disulfide lead to the natural conclusion that thiyl radicals were present at 77°K and to the assignment of the 24.6 kc. cm^{-1} peak. The slow decrease of the peak at 77°K must be caused by an unknown reaction. The position of the isosbestic point, at 28 kc. cm^{-1} , conclusively rules out both recombination reactions $2\text{RS}\cdot \rightarrow \text{R}_2\text{S}_2$ and $\text{RS}\cdot + \text{H} \rightarrow \text{RSH}$. Neither the disulfide nor the mercaptan exhibit any absorption at this low wavenumber.

The splitting of the mercaptan leads to the formation of hydrogen atoms. It has been shown that hydrogenation of the glass-forming isopentane — 3-methyl pentane mixtures used in this laboratory lead to a minor significant decrease in light absorption at wavenumbers around 48 kc. cm^{-1} . This may be explained by assuming that minute quantities of unsaturated compounds were present as impurities. In this connection, it is of interest to quote Potts ⁸, who pointed out that isopentane on standing develops an absorption at 48 to 49 kc. cm^{-1} . It is suggestive to ascribe the decrease in absorption found during the photolysis of the mercaptans in the $50\text{--}46 \text{ kc. cm}^{-1}$ region to a hydrogenation of olefinic impurities by the hydrogen atoms liberated in the proposed reaction.

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