PHOTOLYSIS OF 1-BUTANETHIOL

Peter K. Pearson

ABSTRACT

1-butanethiol was irradiated at 2537 Å. Hydrogen sulfide, butyl disulfide, and the previously unreported dibutyl sulfide were observed in the reaction mixture, in addition to an unidentified compound thought to be identical to the major thermal decomposition product of butyl disulfide. The quantum yields for Bu_2S and $(BuS)_2$ were found to be 0.087 and 1.9 respectively.

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INTRODUCTION

The photolysis of thiols has been studied as early as 1938, when Meissner and Thompson (1) performed a photolysis of ethanethiol in the vapor state, observing the products ethyl disulfide and an uncondensable gaseous mixture roughly 90% H_2 and 10% C_2H_6, with traces of unsaturated hydrocarbons. Measuring a large quantum yield for the disappearance of EtSH (about 10), Meissner and Thompson suggested a chain reaction accounting for the major products:

$$EtSH \xrightarrow{h\nu} EtS\cdot + H\cdot \qquad (I)$$

$$H\cdot + EtSH \longrightarrow EtS\cdot + H_2 \qquad (II)$$

$$2\ EtS\cdot \longrightarrow (EtS)_2 \qquad (III)$$

$$EtS\cdot + EtSH \longrightarrow (EtS)_2 + H\cdot \qquad (IV)$$

$$H\cdot + H\cdot \longrightarrow H_2 \qquad (V)$$

In 1941, Skerrett and Thompson (2) carried to sompletion a photolysis of methanethiol in the vapor state, and found the methyl analogs of the products reported for the ethanethiol photolysis, with the addition of sulfur and the "dimer" C_2H_6, as well as a variable unidentified residue. The quantum yield for the disappearance of MeSH was measured as 1.7.

The next contribution to the list of products was made in 1956 by Haines, Cook, and Ball (3) with their discovery of H_2S in the vapor produced by photolysis of neat butanethiol. The following sequence of reactions was proposed to suit this addition:

$$RSH \xrightarrow{h\nu} R\cdot + \cdot SH \qquad (VI)$$

$$RSH + \cdot SH \longrightarrow H_2S + RS\cdot \qquad (VII)$$

$$R\cdot + RSH \longrightarrow RH + RS\cdot \qquad (VIII)$$

$$RS\cdot \longrightarrow \text{olefin} + \cdot SH \qquad (IX)$$

However, four years later, in 1960, Inaba and Darwent (4) performed various vapor-state photolyses on CH_3SD, and reported that the relative amount of methane in the gaseous product was very much smaller in photolyses which were restricted to less than 1% conversion, concluding that methane is a secondary product, and that hence the reactions

$$MeSH \xrightarrow{h\nu} CH_4 + S \qquad (X)$$

$$MeSH \xrightarrow{h\nu} Me\cdot + \cdot SH \qquad (XI)$$

do not occur to any appreciable extent. (X) had been assumed responsible for both sulfur and methane, (XI) for H_2S.

The presence of a thiyl radical intermediate was strongly confirmed in 1962 when Rosengren (5) succeeded in spectrometrically identifying the butylthiyl radical in a sample of butanethiol irradiated while frozen in a glass at 77°K.

The results of Inaba and Darwent came under fire in 1967 from Steer, Kalra, and Knight (6), whose low-conversion photolyses of methanethiol resulted in gaseous products consisting substantially of methane : roughly 9%, generally independent of pressure or duration of photolysis. Some H_2S was also observed. The same paper observes that the rate of production of disulfide is equal to the sum of the rates of production of H_2 and methane, which strongly suggests that essentially all of the thiyl radicals are consumed by recombination with each other. The major products are then accounted for thus:

$$MeSH \xrightarrow{h\nu} MeS\cdot + H\cdot \quad (90\%) \qquad (XII)$$

$$\searrow \; Me\cdot + \cdot SH \quad (10\%) \qquad (XIII)$$

$$2\ MeS\cdot \longrightarrow (MeS)_2 \qquad (XIV)$$

$$R\cdot + MeSH \longrightarrow RH + MeS\cdot \quad , \text{ where } R = H\cdot\ ,\ Me\cdot\ ,\ \text{or}\ \cdot SH\ .$$

More recently (7,8) Steer *et al.* have suggested a mechanism involving an activated species:

$$2\ EtS\cdot \longrightarrow (EtS)_2^*$$

$$(EtS)_2^* + EtSH \longrightarrow (EtS)_2 + Et\cdot + \cdot SH$$

$$(EtS)_2^* + EtSH \longrightarrow (EtS)_2 + C_2H_4 + H_2S$$

This is where knowledge now stands.

The photolysis of neat butanethiol was of interest to us because of the possibility of using butanethiol as a hydrogen source for photolyses of other compounds, a thiol being attractive because of the very weak S-H bond. The fact that the thiol has its own photochemistry makes it unsuitable for this application, but the previously unreported analysis of the photolysis products of neat butanethiol may contribute substantially to our understanding of thiol photochemistry.

EXPERIMENTAL

Butanethiol was from Matheson, Coleman, & Bell. No attempts at further purification were made. Analysis by vpc indicated an initial impurity of 0.4 mole % butyl disulfide.

Photolysis of 171 ml BuSH was performed in a cylendrical quartz tube 13 cm in circumference and 12.7 cm deep, surrounded by a 2537 mercury lamp, Ultraviolet Products Inc., PCQX1. Nitrogen was bubbled through the liquid during the photolysis.

Identification of products was accomplished by comparing the retention times on one or both of two vpc columns with retention times for known samples. The two columns used for this purpose were Carbowax 15 M 15% on chromosorb W, 6' x $\frac{1}{4}$", at 160°C, and SAE 30, 5%, 10' x $\frac{1}{4}$", at 130°C. The carrier was nitrogen, and a hydrogen flame detector was used.

Assays of products were calculated from the weights of peaks cut out from vapor-phase chromatograms produced with a column of Carbowax 20 M, 20% on Chromosorb W, 6' x $\frac{1}{4}$", at 160°C. Weights of product peaks were compared with the weights of peaks produced by a standard solution 1.96M in butyl disulfide and 0.109 M in dibutyl sulfide. (This standard solution was later judged to be inconveniently concentrated, and a reduction in concentration of a factor of 4 is recommended.) The solvent was heptane.

Lamp intensity was measured using ferrioxalate actinometry. Intensity over the side of the tube was averaged from a number of measurements, and the intensity over the bottom (which represented 10% of the exposed area) was estimated from geometrical considerations to be $\frac{1}{4}$ that over the rest of the surface. The combined error from actinometry and averaging is estimated at 8%.

A further correction is necessary to account for blue light from the lamp, which would have been measured during actinometry without contributing to the thiol photolysis. The fraction of blue light was measured as 25%, using a pyrex filter, and correction was made accordingly.

RESULTS

Four products are observed in the vapor-phase chromatogram of the photolyzed liquid, as depicted in Fig. 1.

The product with the shortest retention time coincided with H_2S on both vpc columns, and was observed to reach its final concentration in the first 8 hours of photolysis, then remain constant while the other products continued to increase in concentration. This behavior is suggestive of a gas which reaches saturation in the irradiated liquid and is thereafter washed out with the nitrogen flow.

The second product to come off the vpc columns had retention times identical to those of dibutyl sulfide. No dialkyl sulfide was found in any previously reported thiol photolysis.

The third product is unidentified. It seemed to appear at a constant rate during the entire photolysis, and hence is probably a primary product. A peak of apparently identical retention times appears in samples of butyl disulfide left standing in brown bottles for periods of several months, so the identity of this product will be of interest to those concerned with maintaining purity in such compounds (3).

The fourth product had retention times identical to those of butyl disulfide. From the literature cited it was to be expected that the disulfide would be the major liquid product. This has been confirmed.

The concentrations of dibutyl sulfide and butyl disulfide were monitored during the photolysis, and their molar concentrations are plotted as a function of time in Fig. 2. It is evident that the rate of increase of each product diminishes toward the end of the photolysis, presumably due to absorption of substantial amounts of light by the disulfide, which has an extinction coefficient roughly 8.5 times that of butanethiol. This effect can be eliminated by use of an "effective time" whose ratio to the actual elapsed time is the same as the ratio of the total light absorbed by the butanethiol to the total light absorbed by all species. This effective time is then proportional to the total amount of light absorbed by the butanethiol. The effect of this correction is evident in Fig. 3.

From the slopes of the lines fitted to the points in Fig. 3, using the light intensity of 7.6×10^{-4} E/l.min , we can calculate quantum yields for the production of butyl disulfide and dibutyl sulfide:

$$\Phi_{(BuS)_2} = 1.9$$

$$\Phi_{Bu_2S} = 0.087$$

DISCUSSION

The production of the dialkyl sulfide, although not previously reported, might have been anticipated from the presence of the alkyl radical as proposed to account for the production of H_2S, e.g. reaction (XIII). Some reactions capable of producing the dialkyl sulfide are:

$$BuSH + BuS\cdot \longrightarrow Bu_2S + \cdot SH \qquad \Delta H = 0 \cdot \qquad (XV)$$

$$BuSH + Bu\cdot \longrightarrow Bu_2S + H\cdot \qquad \Delta H = +\ 18 \text{ kcal} \qquad (XVI)$$

$$Bu\cdot + BuS\cdot \longrightarrow Bu_2S \qquad \Delta H = -\ 65 \text{ kcal} \qquad (XVII)$$

Although (XVIII) is energetically most favorable, the relatively low concentrations of bytylthiyl and especially butyl radicals suggest that (XVIII) probably could not be responsible for the relatively large amounts of sulfide observed. The relative abundance of reactants of (XV), plus the absence of an unfavorable enthalpy of reaction, indicate that (XV) is the major reaction producing the dialkyl sulfide.

The disulfide quantum yield of 1.9 is substantially greater than the recent $\Phi_{(EtS)_2} = 1.26$ reported by Steer et al. for the photolysis of ethanethiol in the vapor state. Since the maximum quantum yield of disulfide obtainable from the reaction sequence (XII), (XIII), and (XIV) is unity, a very substantial number of radicals or disulfide molecules must appear in such reactions

as Steer's activated species reactions or Meissner's originally proposed

$$BuS\cdot + BuSH \longrightarrow (BuS)_2 + H\cdot \qquad \Delta H = +23.$$

Quantum yields for hydrogen, hydrogen sulfide, and butane, not available with the arrangement used here, may clarify the mechanism by which such a large $\Phi_{(BuS)_2}$ is achieved in the photolysis of neat butanethiol.

CONCLUSION

A dialkyl sulfide must be added to the list of products obtained by photolysis of thiols, and yet another product, apparently of high molecular weight, remains to be determined. The unusually high quantum yield found for the disulfide in this photolysis suggests that those poorly-documented reactions responsible for disulfide quantum yields in excess of unity are present to a much greater extent than in previous photolyses, and thus invites further study of those reactions through determination of quantum yields for H_2, H_2S, and C_4H_{10} in this photolysis.

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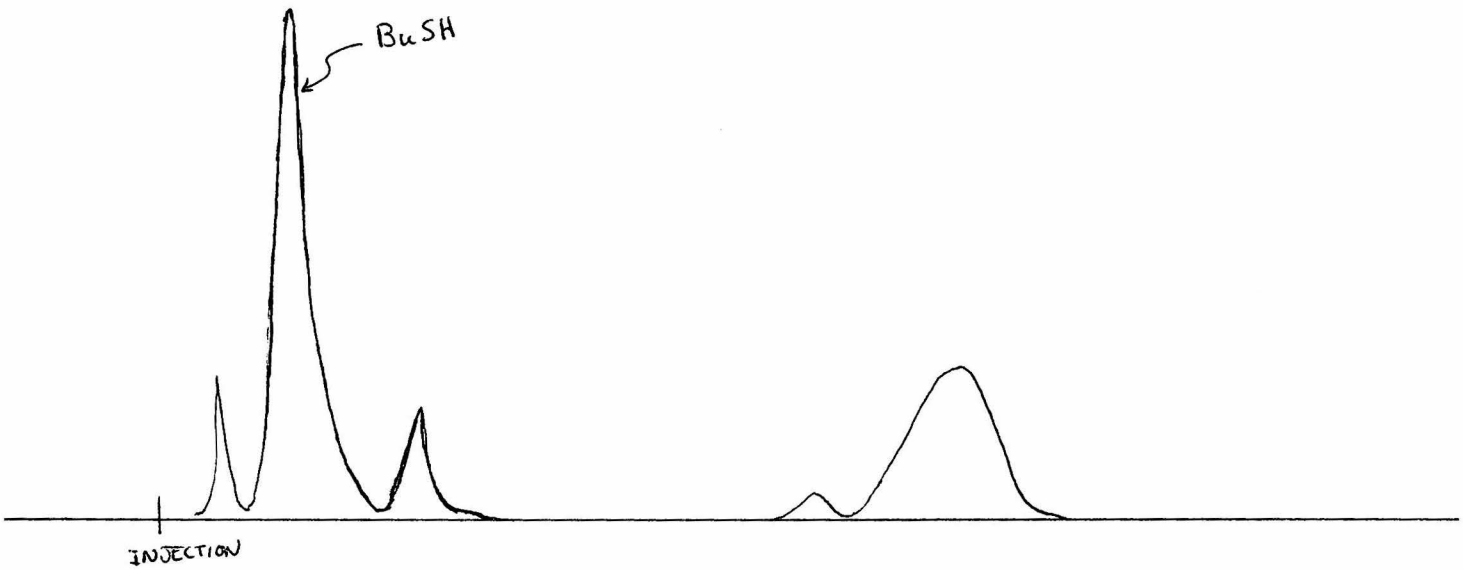

Fig. 1

Typical chromatogram of photolysis mixture during irradiation of butanethiol.

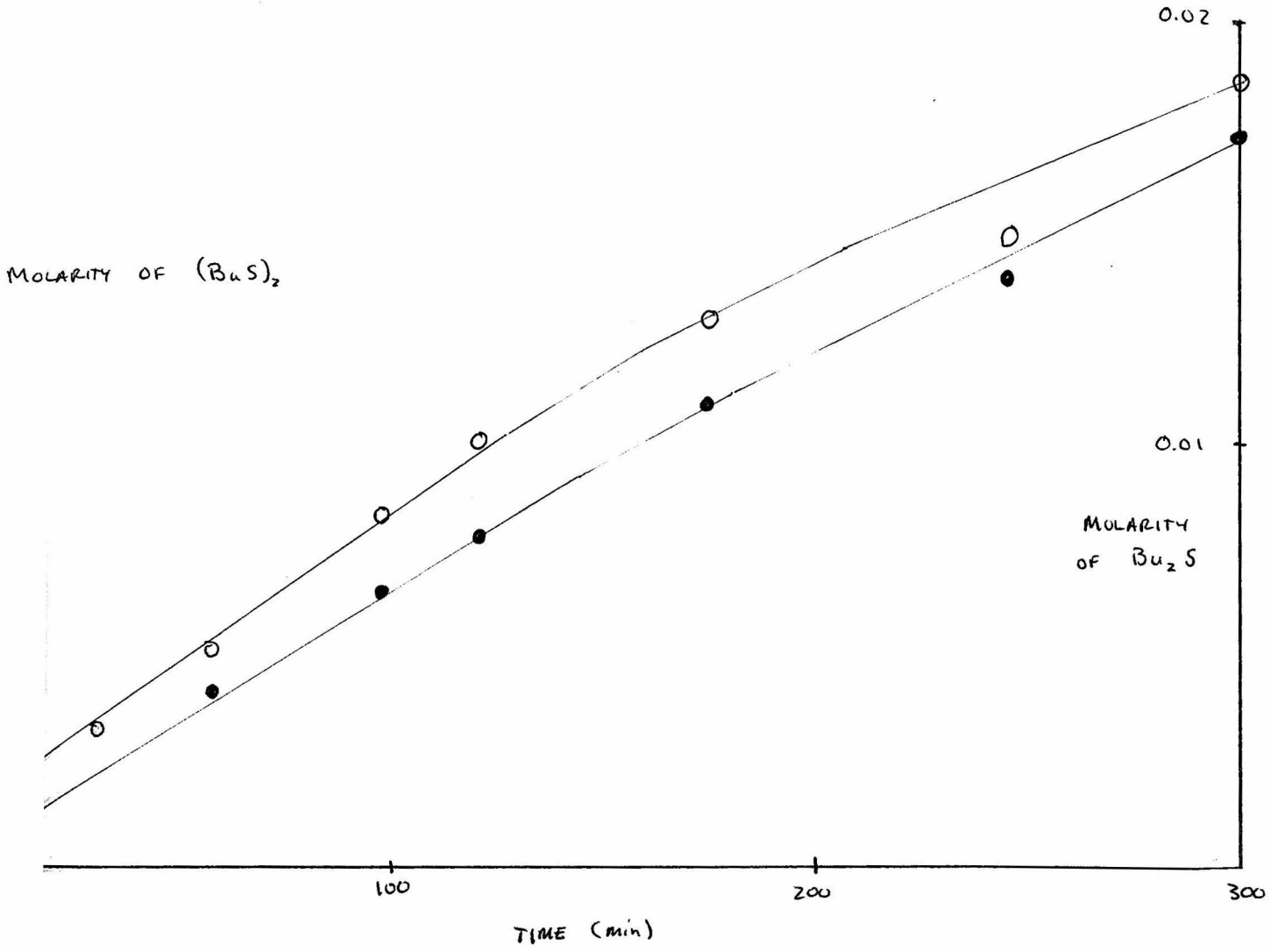

Fig. 2

Concentrations of Bu_2S and $(BuS)_2$ plotted against elapsed time.

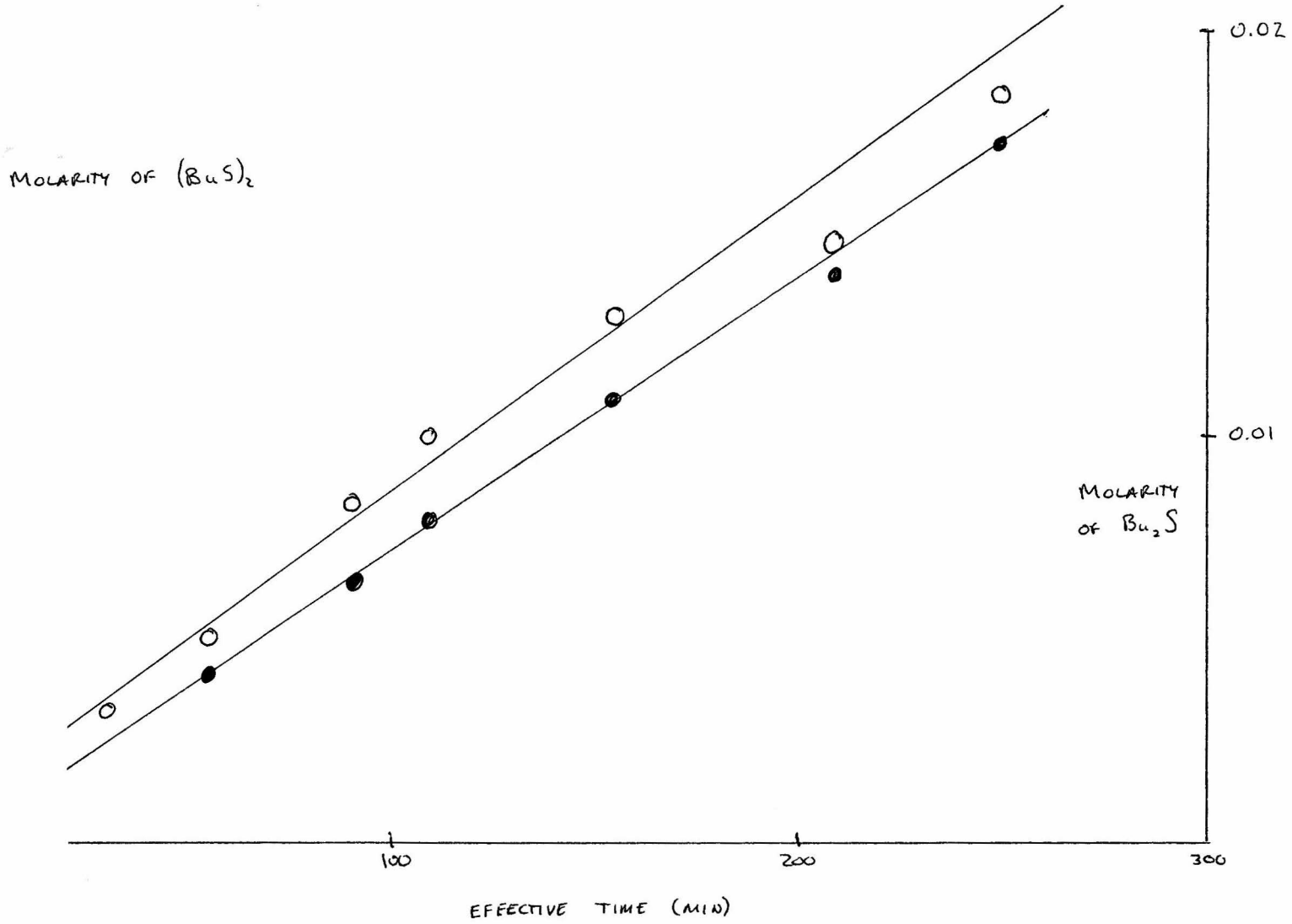

Fig. 3
Concentrations of Bu_2S and $(BuS)_2$ plotted against "effective" time.